Research Project Report

On

"DEMONSTRATION OF OZONE TREATMENT TECHNOLOGY OF INDEGENOUS RAW MATERIALS PULPS AT PILOT PLANT SCALE"

SUBMITTED

TO

RSC-DCPPAI COMMITTEE

CENTRAL PULP AND PAPER RESEARCH INSTITUTE

SAHARANPUR – 247001 (UTTAR PRADESH)

Contents

Nomenclature

A	:	Acid stage
QP	:	chelation followed by peroxide
Z	:	Ozone stage
Ep	:	Alkali followed by peroxide stage
D	:	Chlorine dioxide stage
DTPA	:	Diethylene triamine penta acetic acid
P	:	Peroxide stage
TS	:	Total solid
TSS	:	Total suspended solid
COD	:	Chemical oxygen demand
ODL	:	Oxygen delignification
RAA	:	Residual active alkali
°SR	:	Schopper Riegler

Lists of Table

1. Project Documents

ACKNOWLEDGEMENT

Physical Chemistry, Pulping and Bleaching Division is thankful to Development Council for Pulp, Paper & Allied Industries for awarding the project on **"DEMONOSTRATION OF OZONE TREATMENT TECHNOLOGY OF INDEGENOUS RAW MATERIALS PULPS AT PILOT PLANT SCALE."**

We are thankful to Director, Central Pulp and Paper Research Institute, Saharanpur (U.P.) for providing guidelines for completion of this project. We are also thankful to supporting technical staff and Junior Research Fellows of Physical Chemistry and Pulping and Bleaching Division, Stock Preparation Paper Making & Conversion Division and Environmental Management Division for their cooperation.

(Priti S Lal)
Scientist E-II
Head PCPB Div.
CPPRI Saharanpur

CERTIFICATE FROM THE INVESTIGATOR

For Office Use Only

Project Title: **Demonstration of Ozone Treatment Technology of Indigenous raw material pulp at Pilot Plant Scale**

Agency: Central Pulp & Paper Research Institute, Saharanpur (U.P.)

Participating: Nil

Total Project Cost (Rs.) 69 Lac.

Project Duration: 24 Months Starting From April, 2018

Remarks: The production of bleached pulp applying clean and green technology is of high demand. In spite of availability of best equipment and technology, its adoption for Indian Pulp and Paper Industry needs to scale up the modern bleaching technology according to the Indian system. Hence it is important to equip the CPPRI with the new technology at laboratory as well as pilot plant scale in order to meet out the demand of Industry.

Date: Name & Signature of the Investigator

Place: Saharanpur.

CERTIFICATE FROM THE INVESTIGATOR

Project Title: Demonstration of Ozone Treatment Technology of Indigenous raw material pulp at Pilot Plant Scale

I/We agree to abide by the terms and conditions of the grant/support. To that effect we have also signed the necessary bond with CPPRI Research Steering Committee for due performance of the terms and conditions laid down.

1. The research project work proposed in the scheme does not in any way duplicates the research work already done and being carried out elsewhere on the subject.

2. The present scheme is not combined with any other scheme financed by the council, Central and State Government, University or Private Institutions of their own funds.

3. I/We did not submit the project proposal elsewhere for financial support.

4. I/We have explored and ensure that equipment and basic facilities (enumerated in the proposal) will actually be available as and when required for the purpose of the project. I/we shall not request financial support under this project, for procurement of these items.

5. I/We undertake that spare time on permanent equipment (Listed in the proposal) will be made available to other users.

6. I/We enclosed the following materials:

Item	Number of Copies

a. Endorsement from the Head of Institution	One (In original attached with one copy of the proposal)
b. This certificate from investigator (s)	One (In original attached with one copy of the proposal)
c. Copies of the proposal in the format	10

Date:

Name & Signature of the Investigator

Place: Saharanpur.

ENDORSMENT FOR THE HEAD OF THE INSTITUTION

Project: - Demonstration of Ozone Treatment Technology of Indigenous raw material pulp at Pilot Plant Scale

1. Certified that the institution welcomes the participation of Mrs. Rita Tandon, Sc. G as the Principal investigator (Project leader).

2. Certified that the equipment and the other facilities as enumerated in the proposal as per the terms and conditions of the grant will be extended to the investigators throughout the duration of the project.

Dated:

Place: Saharanpur ((U.P)

DIRECTOR

1. **Project Proposal**

i	**Title of the project**	:	Demonstration of Ozone Treatment Technology of Indigenous raw material pulp at Pilot Plant Scale.
ii	**Broad (focused) Area**	:	Ozone bleaching technology.
iii	**Project Duration**	:	2 Years
iv	**Institution/organization**	:	Central Pulp and Paper Research Institute
v	**Actual location where research project work**	:	CPPRI
vi	**Principal Investigator**	:	Name: Dr. Rita Tandon Designation: Scientist - G Department: Physical Chemistry, Pulping and Bleaching Division Address: CPPRI,P.O.Box-174, Saharanpur-247001 (U.P.)
	Other Investigators		Name: Dr. Priti. S. Lal Designation: Scientist E-II Department: Physical Chemistry, Pulping and Bleaching Division Address: CPPRI,P.O.Box-174, Saharanpur-247001 (U.P.) Name: Dr. Arvind Kumar Sharma Designation: Scientist -B Department: Physical Chemistry, Pulping and Bleaching Division Address: CPPRI,P.O.Box-174, Saharanpur-247001 (U.P.)

			Name Mr. Mohd Salim Designation SSA Department Environment Management Division Address CPPRI,P.O.Box-174, Saharanpur-247001 (U.P.) Name Mr. Kumar Anupam Designation SSA Department Chemical Recovery CPPRI,P.O.Box-174, Address Saharanpur-247001 (U.P.)
vii	**Name and address of person/institution interested in the outcome of the project**		Indian Agro-based medium /small Paper Mills

Introduction and Background

Reduction of fresh water usage and limitation in effluent load are major driving forces for long-term sustainability in pulp production. Ozone has proven to be one of the best green oxidant for bleaching of unbleached pulp in order to reduce AOX, COD emission and fresh water usage. The need to lower operating costs and comply with always stricter global ecological regulations has force the industry into upgrading its bleaching technology. Ozone bleaching has successfully proven to be an economical and sustainable alternative bleaching chemical for wood pulp, but its efficacy for agro-residue pulp is yet to study.

A project for laboratory scale studies on ozone treatment approved by CESS committee was carried out during 2009-2012 on “efficacy of ozone pretreatment of Indigenous raw material Pulp” by Central Pulp and Paper Institute Saharanpur. The findings are very encouraging and there is strong need of development and demonstration of ozone bleaching technology at pilot plant scale.

i. Objectives of the Project

Fabrication of pilot scale ozone reactor for ozone treatment of Indigenous raw materials pulp mainly agro-based raw materials used by small and medium sized pulp and paper Mills.

ii. Relevance of the project

The laboratory scale studies carried out on ozone bleaching of wood and agro-based raw material and the findings needs further scale up of the technology at pilot plant scale. There is strong need of infrastructure development i.e. fabrication of pilot scale ozone reactor, which may conduct experiments at pilot scale of 2-5 kg capacity and not available anywhere in India.

The technological simulation of pilot scale ozone bleaching technology with commercial available ozone reactors will help in development of understanding of pulp mixing during ozone bleaching. This further will help in ozone reactor design for small and medium pulp and paper mills at commercial scale. Outcome of the project will be beneficial to Indian agro based pulp and paper mills in attaining better strength of pulp and cleaner production by adopting ozone based bleaching sequence.

iii. Literature Survey and status of work already done

Very few articles are available in literature on ozone bleaching of agro-based raw materials viz. bagasse and wheat straw. However the ozone bleaching of softwood and hardwood pulp is vastly reported in literature. The TCF bleaching of pulp using ozone is reported in literature which proves its efficacy at mill scale. Not only ozone help in reduction of pollution load but also economic too.

iv. Lines of Investigation;

- Detailed survey on design of pilot or mill scale reactor and preparation of reactor drawing before initiation of fabrication process for pilot scale reactor of 2-5 kg capacity.
- Fabrication of pilot scale reactor for ozone treatment and installation of same at CPPRI or any designated agro-based mill.

- ECF (ODEpD) bleaching of unbleached pulp and its comparison with ozone based ECF/TCF sequence (OZDEpD; O(QZ)PP; OP(QZ)PP sequences at pilot scale.
- Evaluation of pulp properties after bleaching of pulps.
- Comparison of effluent properties of ECF and TCF bleaching processes and comparative analysis of ECF and TCF bleach effluent for various parameters to evaluate the impact on reduction in pollution load.
- Study on addition of ozone stabilizers and cellulose protector for improvement of ozone treatment efficiency.

Compilation of data and preparation of report and dissemination of findings

v. Expected Outcome

- Study will provide the pilot scale facility of ozone bleaching for pulp of Indian raw materials viz, hardwood and agro residues.
- Ozone is non chlorine bleach chemical. The effluent after ozone bleaching can be used in BSW and other stages since it does not contain non process elements. The findings of the project will help in direction of bleach plant closure partially or completely.
- Optical properties of the bleached pulp will be improved significantly compared to the pulps produced with conventional bleaching sequence as oxidation potential of ozone is the highest among all bleaching chemicals. Ozone bleaching of pulp may overcome the issue of brightness ceiling for different agro residue based raw materials.

2. Introduction of Ozone Bleaching

The pulp and paper industry is exploring ways to reduce its impact on the environment. Reducing the formation of chlorinated organic compounds and the volume of discharged effluent are key areas for improvement. Bleaching with oxygen-based chemicals can serve the pulp and paper industry well in meeting both of these objectives. Ozone (O_3) was introduced in the bleaching of chemical pulps in early 1990s. Ozone is one promising oxygen-based alternative. Since then, about 30 bleach lines containing ozone have been installed. The first industrial pulp bleaching line including an ozone stage started ~ 25 years ago. Among those 22 mills, 16 produce solely hardwood pulps, 4 produce both softwood and hardwood pulps while SCA in Östrand (Sweden) and Rosenthal in Blankenstein (Germany) produce exclusively softwood pulp (Lindholm 1990, Lind storm1990 Rangnar et.al, 2000) .

Ozone bleaching is efficiently used on hardwood and softwood pulps, on kraft and sulphite pulps dedicated to all kinds of final applications. Pulp producers do not always evaluate the significant ecological advantages of ozone-based bleaching sequences over the traditional ECF bleaching sequence D0-Eop-D1-D2 (or its variants). Sweden, Brazil, Japan, Finland and USA are among the countries where ozone stage in bleaching sequence (Parker et. al.1991, Major et.al, 2005).

Ozone bleaching of agro pulps is considered as one of the Best Available Technology (BAT) for environmental point of view as a greentechnologies. it is a well-proven technology with significantly lower operating costs.

With increasing regulatory pressure and growing market demand for better products, the pulp and paper industry faces many challenges and is looking for new ways to improve environmental and process performance, while maintaining economic feasibility. By choosing ozone bleaching technology in their bleaching process, a number of pulp and paper mills have already achieved these benefits in various parts of the world. Ozone is now used by more than 30 bleaching fibre lines are producing 8 million tons of ozone bleached pulp for both softwood and hardwood kraft pulps (Metais 2017, Ribeiro et.al, 2014). None of the agro-residue based pulp and paper mill is presently using ozone as bleaching chemical.

Ozone (O_3) is produced from oxygen (O_2) in an electrical field at a concentration of 12% by weight according to Figure1: Production of 1kg ozone requires a maximum of 10 KWH power and 8.3 kg of oxygen(Wyk, Madhvan, Matais 2017)

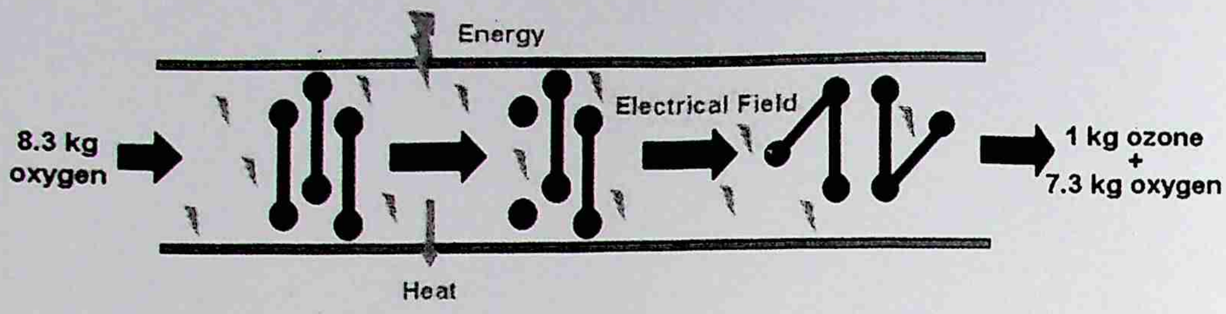


Figure1:- Ozone formation in an electrical field

.Ozone is an electrophilic, nonlinear, strong oxidizing agent with an oxidation potential of-2.07 eV that promotes reaction with functional groups in the lignin present in lignocellulosic materials which are used for papermaking. Aliphatic double bonds conjugated to the aromatic rings in stilbene, styrene, and enol ether structures present in lignocellulosic raw materials will form epoxides or ozonides, or further form carbonyl groups and hydrogen peroxide when reacts with ozone according to Figure2. It is more selective toward lignin compared to carbohydrates but formation of intermediate radicals during ozone bleaching has detrimental effect on carbohydrates (Moldenius and Nutt et al. 1995, Zou et al. 2000, Rice and Netzer 1982). It was found that ozone appears to be more efficient than chlorine dioxide and hydrogen peroxide in inducing the formation of carboxylic acid from residual kraft lignin (Pryke 1991, Esteve et al. 2020).

Formation of radicals during ozone bleaching of pulps promotes the unwanted attack on carbohydrates and decomposition of ozone in water. Reaction of ozone with the carbohydrate fraction of pulp reduces the pulp viscosity thereby the undesirable decline in strength properties of paper (Ragnar et al. 1999, Kawakami and Pikka 2000). The pulp viscosity reflects the degree of polymerisation of the cellulose chain. Reaction of ozone with lignin generates highly reactive radicals that can lead to cellulose depolymerisation. According to researchers Ozone itself found to be 106 times more reactive to lignin than to carbohydrates. However, the by-products from those reactions of are easier to react with carbohydrates (Hassan and Barbary 2003, Chirat and Lachenal 1997).

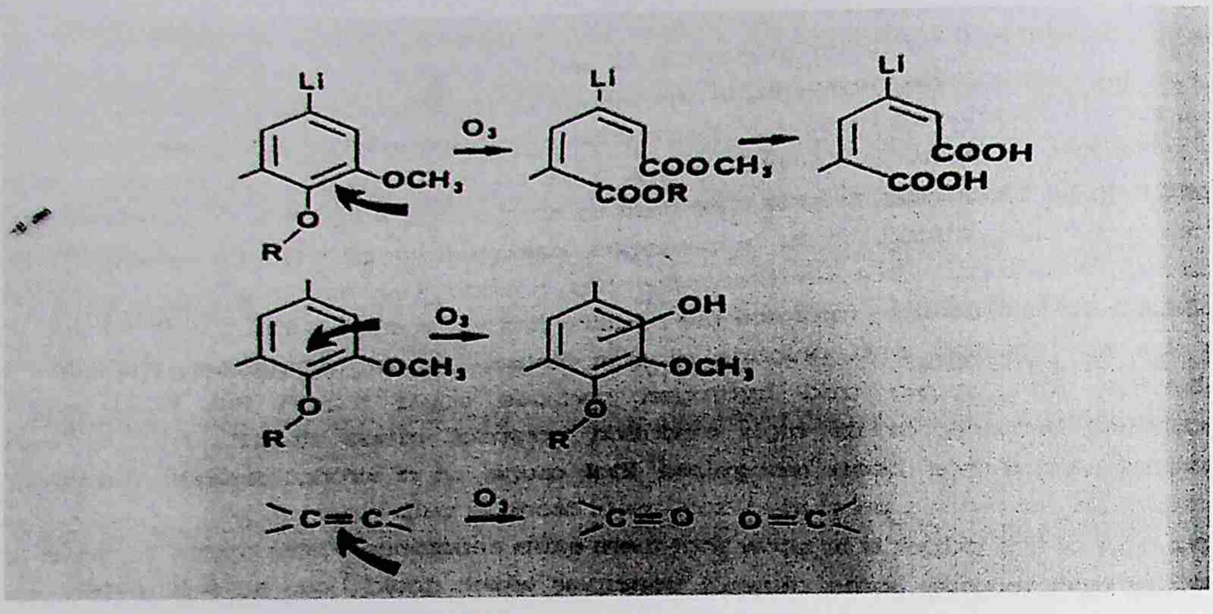


Figure2: Main lignin reactions with ozone during ozone bleaching

The nature of this reaction leads to a hypothesis that pulp with high lignin will sustain more on viscosity loss than low lignin pulp. Ozone also oxidizes cellulose, possibly subjecting it to subsequent depolymerisation under alkaline conditions (Ragnar et al. 2005, Hannuksela, Holmbom, Lachenal 2004). Ozone is also decomposed by the catalytic action of transition metal ions present in pulp and forms hydroxyl, hydroperoxyl and superoxide anion radical intermediates which may be detrimental to the carbohydrates (Deepika et. al, 2019, Gierer and Imsgard 1977). Ozone bleaching of pulps having low physical strength properties, such as agro residue based raw material pulps, is supposed to be more critical. Higher degradation of carbohydrates during ozone bleaching of agro residue pulps may further deteriorate the physical strength properties and make the pulp unusable for papermaking (Ghosh 2006, Douglas 1987).

The detrimental effects of ozone can be avoided by using different chemicals that work as carbohydrate protectors. Substantial research has been carried out for discovering suitable carbohydrate protector for ozone bleaching of pulps, mostly on hardwood and softwood pulps (Freire et al. 2003, Degussa 1999). A lot of chemicals have been reported to improve selectivity of ozone for different pulps. Based on the cellulose lose protecting mechanism, these chemicals may be organized as radical scavangers like ethanol (Liebergott et al. 1978), methanol (Kamishima et al. 1977, Kamishima et al. 1983, Roncero et al. 2001), mannitol

(Jablonsky et al. 2005, Jablonsky 2009); chelating agents like dimethyl sulfoxide (Kamishima et al. 1977, Roncero et al. 2001), ethylene diamine tetraacetic acid (Roncero et al. 2002); ozone stability enhancers like acetic acid (Roncero et al. 2002), sulfuric acid (Roncero et al. 2002), sulfamic acid (Kamishima et al. 1977, Roncero et al. 2001), ammonium molybdate (Agnemo 2002), oxalic acid (Kamishima et al. 1982, Roncero et al. 2003); oxidative chemicals like peracetic acid (Rudie,2012, Fuhrman et al. 1997, Saake et al. 1998, Jablonsky et al. 2005), sodium hypo chlorite (Suchy et al, 2002) and other chemicals like cationic potato starch (Jablonsky et al. 2005), dimethyl sulfoxide (Kamishima et al. 1977, Roncero et al. 2001), dimethyl formamide (Kamishima et al. 1977), urea (Kamishima et al. 1977), and zirconium (IV) propoxide (Jablonsky et al. 2005). The use of ozone for bleaching of pulp will increase significantly if a cost effective cellulose protector is found. Very little work has been reported either on ozone bleaching alone or using different cellulose protectors in ozone bleaching of agro residue pulps (Sixta et al. 1991). The main five processes variables that influence the effectiveness and selectivity of ozone delignification are pH, consistency, time, temperature and ozone dose, metal ions affecting the ozone bleaching of agro pulps by studying their effect on three pulp parameters kappa number, brightness and viscosity (Tripathi et al. 2019a), . A rapid and efficient transfer of ozone into appropriate fibre constituents is very important to enhance ozone-lignin reaction instead of cellulose decomposition (Tripathi et al. 2019b).

Ozone bleaching conditions for agro pulps were further optimized. In the present study efficacy of chemicals like pentaacetic acid (DTPA), methanol, is investigated as protector of carbohydrates during ozone bleaching of agro pulps. These additives were selected based on their efficacy reported earlier on different pulps for improving viscosity, brightness and reducing the kappa number during ozone bleaching. This project activities reveals the effects of using different additives in ozone bleaching on delignification efficiency, selectivity of ozone, bleachability of pulp and effect on chain scission number. These two parameters ie. Kappa number and pulp viscosity will be used to express the effectiveness of ozone delignification and its selectivity. The results of the project will be relevant to the pulp and paper industry using ozone as one of the bleaching sequence. This study will be more beneficial for agro based paper mills planning to improve productivity and pulp quality (Tripathi, Bhardwaj and Ghatak 2019).

Much of early years, ozone bleaching works on low (0.5–3%) and high (30-40%) stock consistencies. Low consistency allows optimum mixing. In the high consistency maximum exposure of fibre surface to ozone is achieved by fluffing to separate fiber aggregates to the greatest extent possible. The most efficient delignification for ozone bleaching occurs near pH 2. In high consistency ozone bleaching, acid treatment prior to bleaching can remove metal ions from pulp, while acids brings H+ that replace M+ in the pulp (Tao et al. 2011). Alkali extraction stage after ozone bleaching is purposed to reduce kappa number of ozone-delignified pulp. Alkali has an important role to remove lignin from pulp (McDonough 1986, Hastachy 2009, Afsahi etb al. 2015).

The industrial use of ozone has already undergone a long string of improvements and developments. Like other new technologies, ozone bleaching did not immediately reach its optimal technical efficiency but faced several issues during its early years. Achievements of ozone bleaching have improved year in year out and it is now a well proven technology for bleaching of unbleached pulp (Asgari and Argyropoulos 1998, Pandey et al. 2012).

Eucalyptus pulp is being bleached as single species or as a mixed hardwood pulp, with ozone in more than 10 mills around the world including Brazil bleached as a single Eucalypts, Japan, Australia, India and Europe. Most of these mill use ĖCF sequence with ozone as such as

1. ZEpDP where Z is a high consistency ozone bleaching stage followed by dilution to medium consistency and allow for an extraction stage e stage to take place without intermediate washing.
2. Z/DEOP-D where Z/D as a medium consistency ozone bleaching stage Z followed directly by a chlorine dioxide stage D with intermediate washing.

- ECF (ODEpD) bleaching of unbleached pulp and its comparison with ozone based ECF/TCF sequence OZDEpD; O(QZ)PP; OP(QZ)PP sequences at pilot scale.
- Evaluation of pulp properties after bleaching of pulps.
- Comparison of effluent properties of ECF and TCF bleaching processes and comparative analysis of ECF and TCF bleach effluent for various parameters to evaluate the impact on reduction in pollution load.

3. Material and methods

Bagasse

Pulp from sugar cane (Sachharum officinarum) residue was commonly known as bagasse. About 4.25 million hectare Cane sugar produced in India by which 70-ton/hectare yield of cane sugar. Cane sugar crushed by sugar factories 180 million tons and average duration of season 150 to 180 days. Bagasse is used about 7.1 million tonne per annum for paper production in India. Major sugarcane growing states are Utter Pradesh, Maharashtra, TamilNadu and Karnataka. Bagasse is the solid fibrous material left after the extraction of juice from the sugar cane. Bagasse, a by-product of the sugar industry that constitutes about 30% of cane processed for production of sugar is used as a fuel for generation of steam and power to meet the process requirements. Depending upon the energy efficiency, sugar mills also save bagasse ranging from 4% to 10% on cane (Statista.com,). The saved bagasse is utilized for production of pulp, paper and particleboard. The transportation of bagasse to the paper mills poses serious problems keeping in view the volume of bagasse etc. Hence, the paper plants, which are situated near the sugar mills, are only able to partly utilize bagasse as a raw material for production of paper. (Sugar Mill Association). Bagasse is preventing global warming and forest decreasing and raising new industry, making a contribution to economic self-supporting developing countries. Bagasse paper will also contribute to conserve global environment, and then you will be recognized as an esteemed company who is well aware of it (Bisht and Bisht 2016, Liu et al. 2018). Bagasse from sugar mill has substantial pith content ~25-30%.the depithing of bagasse is an essential step and preferably carried out at sugar mill site. The depithing is carried out by dry or moist process. The fiber separated is used for production of chemical grade pulp production.

Wheat straw

Wheat straw an agro residual raw material is available in abundance, where ever wheat is the major food crop. Its use as fodder to feed animals is well known and if in surplus, burned in the field. The use of wheat straw as a potential source of paper making fiber is well established. The small and medium size paper mills in India make writing and printing paper from wheat straw. The random estimates suggest that 3.0 tons of wheat straw is produced per ton of wheat. The annual production of Wheat straw is about 90 million tones as Crop production and about 1200 million tones is the residue generation as waste. Wheat straw is used for fodder and thatching and therefore less quantity was available for paper industry for paper and board production (papermart.in). The crop residue ratio of the wheat straw is about 1.50. Out of this less than 1% is being used by paper industry.

3.1 Raw materials preparation

The depithed bagasse and wheat straw were collected from agro based pulp and paper mill. Finally, the raw materials were air dried and then stored in sealed polythene bag for pulping. The moisture content was determined by the difference in weight as received and after drying at 105± 20 °C .

3.2 Pulping experiments

Kraft and Soda pulping of depithed bagasse and wheat straw pulping experiments were performed in autoclave digester consisting six bombs of 2.5 l capacity, rotating in an electrically heated air/polyethylene glycol bath under pulping conditions which are shown below:

Table 1: General pulping conditions for depithed bagasse and wheat straw

S. No.	Particulars	Unit	Depithed bagasse	Wheat straw
1.	Sulfidity of white liquor	%	20	-
2.	Bath ratio	-	1:5	1:5
3.	Time to temperature (Ambient -165°C)	hr.	2	2
4.	Time at temperature. (165°C)	hr.	1.5	1.5
5.	H - factor	-	830	830

3.2.1 Active Alkali

Pulping converts depithed bagasse and wheat straw into separate fibres by the chemical reaction between lignin and the active chemicals in case of bagasse whereas NaoH in case of wheat starw in the cooking liquor, NaOH and Na_2S (expressed as Na_2O) in order to get pulp kappa 12-14 and the liquor/materials ratio was 5:1.

3.2.2 Kappa Number

Depithed bagasse and wheat straw were cooked to a comparable grade of pulp by kraft process and soda process to get (Kappa number range of 12-14). It is a measure of the lignin content (bleach ability) of pulp, hardness and degree of delignification. It is the volume (in ml) on 0.1 N Potassium permanganate solution consumed by 1 gm of moisture free pulp.

3.2.3 Screened yield

This is the percentage of unbleached pulp obtained from moisture-free chips. It is obtained by dividing the weight of dry unbleached pulp (after removing rejects) by the weight of the materials and multiplied by 100.

3.2.4 Rejects

Rejects is the uncooked material obtained after cooking the raw material. It is expressed as percentage of dry raw materials taken for pulping. Lower reject value preferred.

3.3 Bleaching of pulps

Elemental chlorine free (ECF), Light ECF and total chlorine free (TCF) bleaching experiments of Oxygen delignified bagasse and wheat straw pulps were carried out to achieve final brightness ~ 85 % ISO. All the bleaching stages will carry out at various pulp consistencies. Following bleaching conditions were maintained during the bleaching for each sample:

3.3.1 Oxygen Delignification of pulp

In order to get the highest possible oxygen delignification (OD) degree of unbleached bagasse and wheat straw pulp in a single stage OD system the optimum level of oxygen pressure and temperature should be reached in the reactor under alkaline medium to achieve maximum reduction in kappa number and brightness value of the resultant pulp. Oxygen delignification of bagasse and wheat straw pulp samples was carried out in quantum mixer. Pulp 250 gm was taken for each oxygen treatment in reactor vessel. After mixing with sodium hydroxide to the pulps, the pulps were preheated in the microwave oven to 90ºC and pH of the pulp was determined. Volume of the reactor vessel is 3.5 litres. The preheated pulps were placed in reactor vessel through the cylinder under the general conditions given in Table 2.

Table 2 : General conditions of the laboratory oxygen delignification

S.No.	Oxygen delignification stage	1^{st} stage
1	Consistency (%)	10
2	NaOH (%)	2.0
3	O_2 pressure(kg/cm^2)	5.0
4	Temperature(°C)	90
5	Retention time (min.)	90

Table3: Bleaching conditions for different bleaching sequence

Parameters	O stage	OP stage	Q stage	Z stage	D1 stage	Ep stage	P1and P2 stage	D2 stage
Consistency, %	10	10	5	15	5	10	10	10
Reaction time, min	90	90	60	15	60	90	90	180
Reaction temp, ^{0}C	90	120	50	40	80	70	90	80
End pH	11-12	11-12	5-6	2-3	2-3	11-12	10-11	3-4

3.3.2 Chlorine dioxide stage:

Chlorine dioxide bleaching chemical, 40-50 gpl strength, was prepared in the lab using sodium chlorite, acetic acid, and sodium acetate. This solution was added to pulp. The pulp inlet pH of 2-3 was maintained in the D_0 stage, whereas 3-4 in the case of D_1 stage. Chlorine dioxide D_0 and D_1 stages were performed in the polyethylene bags using a water bath. The bleaching chemical of chlorine dioxide was used as D in D_0 and D_1 bleaching stages at 2% and 1%, respectively.

3.3.3 Extraction followed by Hydrogen peroxide stage:

Chlorinated lignin derivatives are to be extracted out of the pulp by addition of alkali and hydrogen peroxide chemicals. The alkali and hydrogen peroxide chemical charges were applied at 2.5% and 1% respectively with 2 -3 kg of oxygen pressure. After giving a certain amount of retention time, the pulp was washed.

3.3.4 Acid stage (A):

Prior to ozone treatment, the pulp was thoroughly mixed with water and sulfuric acid then preheated to the desired temperature in a microwave oven and placed into a temperature-controlled heating bath to maintain a pulp consistency of 5 % for 45 min. After the completion of the desired reaction time, about 300 mL of liquor was squeezed out from the pulp for pH analyses. The acid treated pulp was taken for further bleaching experiments.

3.3.5 Ozone Stage:

Ozone experiments were performed in a quantum reactor with a 250 grams oven dried mixed pulp sample maintaining pulp consistencies of 15-20% at pH 2.0-2.5 and an ozone reaction time of 5.0 min with a 10 min retention time. Each pulp sample was acidified to pH 2.5 with 4N H_2SO_4 and placed into the mixer bowl then supplied with the required amount of ozone injected into the bowl through the ozone generator. The ozone concentration in the stream was measured with the titration method as unreacted ozone from the pulp was collected in a 5% KI solution, after which the residual ozone concentration was determined. The ozone consumed by the pulp was calculated as the difference between applied and residual ozone. At the end of the reaction, the unwashed ozone treated pulp was washed with water for a further bleaching stage.

Ozone strength determination:

The strength of ozone was determined using the following steps; Take 200 ml of KI solution and 100 ml 4N H_2SO_4 solution are added in impinger glass bottle with bubbling the sampled air at low flow rate ; a second impinger glass bottle is joined in series as a guard detector for ozone transfer and reaction in the bottle; ozone generator at a flow rate 5LPM gas pass in acidified KI solution for 1 min immediately titrating against standard solution of freshly prepared 0.1 N $Na_2S_2O_3$ using starch 0.5ml of the starch indicator until solution pale yellow color become colorless.

Ozone concentration in gpl = 24 x volume of $Na_2S_2O_3$ in ml x 0.1Normality of $Na_2S_2O_3$ divided by initial volume of ozone gas in liter

3.3.6 Chelation (Q)

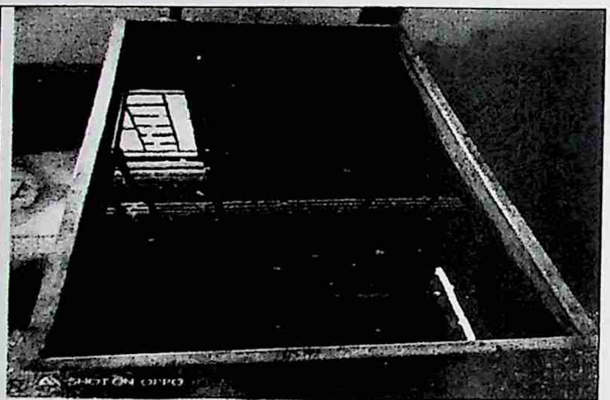
The chelation stage for metal removal was carried out in polyethylene bags with under the condition shown in the tables of results. The pulp samples were thoroughly mixed with water, sulphuric acid and DTPA and preheated to the desired temperature in a temperature-controlled heating water bath. After the completion of the desired reaction time about 250 ml of liquor was squeezed out from the pulp for pH analyses.

3.3.7 Peroxide Stage:

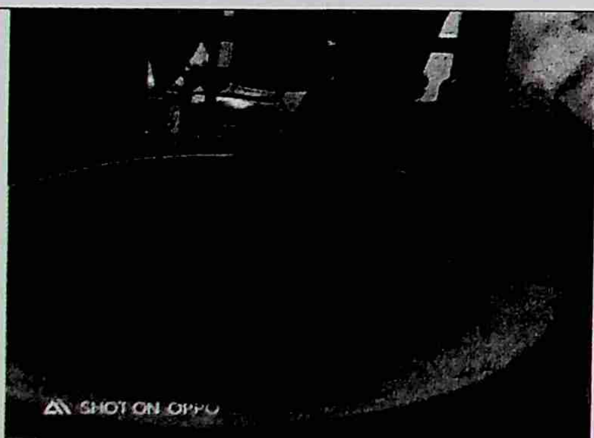
The peroxide stage of bagasse and wheat straw pulps were carried out in laboratory under various conditions. The desired charges of hydrogen peroxide and sodium hydroxide were added in pulp after that chemical mixed pulps were kept in water bath to get desired temperature. The initial pH of the pulp slurry was taken. After completion of reaction time, the pulp was transferred to the pulp discharger and 200 mL of liquor was squeezed out from the pulp for pH and residual peroxide analysis.

Laboratory Pulping and Bleaching Facility

1. Pulping unit



2. Bomb cooling tank



3. Pulp washing Unit

4. Screening Unit

3.4 Pulp characteristics

3.4.1 Brightness

Brightness is a commonly used industrial term for the value of reflectance factor when blue light is used at 457 nm wave length. Brightness values of pulps provide an excellent measure of the maximum whiteness that can be achieved.

3.4.2 Viscosity

It gives an indication of the average degree of polymerization of the cellulose. It also gives a relative indication of the degradation (decrease in cellulose molecular weight) resulting from the pulping and/or bleaching process.

3.4.3 Post color number:

The Post color (P.C.) number is defined as the brightness reversion of bleached bgasse and wheat straw pulps [18] and is calculated by brightness before and after aging. The aging of bleached pulps were determined by putting the pulps sheet in an oven at 105 °C for 4 hours as per TAPPI UM200. The post colour numbers of bleached pulps were calculated as per equation 1:

$$\text{P.C. number} = \left(\frac{(1-\text{R2})^2}{2\text{R2}} - \frac{(1-\text{R1})^2}{2\text{R1}}\right) * 100$$

Where R1 is the brightness before the aging test and R2 is the brightness afterward

3.5 Physical strength properties of Pulps

The bleached hand sheet of 60 GSM were prepared with British sheet former machine according to the ISO 5269.1:2005 standard to measure tensile index (ISO 1924), tear Index (ISO 1974). Hand sheets were prepared from bleached pulp of bagasse and wheat straw & pressed in lab press and keep for 24 hours to air dry at atmospheric condition. Bleached pulps sheet were kept for conditioning at temperature 27± 10C and relative humidity 65± 10C just before measure the physical strength properties.

3.6 Combined bleached Effluent

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

3.6.1 pH

At a given temperature the intensity of the acidic I basic character of a solution is indicated by pH. Every phase of water supply & wastewater treatment e.g. acid base neutralization, water softening, precipitation, coagulation, disinfectants & corrosion control is pH dependent.

3.6.2 Total Suspended Solid, TSS

Presence of high concentration of TSS may adversely affect the effluent quality both from aesthetic considerations and also from point of view of its discharge into the recipient bodies.

The suspended solids when discharged into streams get degraded over a period of time under aerobic conditions resulting in depletion of dissolved oxygen in water while when degraded under anaerobic conditions methane generation may take place which is toxic to aquatic life.

Similarly, when discharged on land they may clog the soil pores adversely affecting the soil properties and making it unsuitable for cultivation.

3.6.3 Total dissolved solids, TDS

Solids may affect water or effluent quality adversely in a number of ways. Highly mineralized water is unsuitable for many industrial applications. TDS analysis is important for biological & physical waste water treatment process. TDS is material residue left in the vessels after evaporation of sample in an oven at defined temperature.

3.6.4 Chemical Oxygen Demand, COD

The chemical oxygen demand (COD) is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant COD can be related empirically to the Biological Oxygen Demand (BOD), organic carbon, or organic matter.

3.6.5 Biological Oxygen Demand, BOD

BOD is the measure of degradable organic material present in a waste water sample and can be defined as the amount of oxygen required by the micro-organisms in stabilizing the biologically degradable organic matter under aerobic conditions at specified conditions.

Generally, the incubation period in for BOD determination is 5 days at 20° C, in Scandinavian countries it is 7 days. Recently CPCB has approved BOD determination with incubation period of 3 days at 27° C.

3.6.6 Absorbable Organic Halides, AOX

AOX measures the amount of chlorine associated with the organic compounds, which is absorbable on to the activated carbon. At present reduction and control of this parameter is on the top agenda of every pulp & paper industry. The source of AOX generation is use of elemental chlorine in bleaching sequence. Chlorine dioxide also contributes in AOX formation but in lower amount.

4. Result and Discussion

4.1 Effect of partially and eco- friendly ozone bleaching on pulp characteristics & physical strength properties bagasse pulp

Table 7 results reveals that unbleached bagasse pulp with a kappa number 13.6, a intrinsic viscosity of 1013 cc/gm and brightness of 30.1% (ISO) bleached with ODEpD, OZDEpD, O(QZ)PP and OP(QZ)PP bleaching sequences. The pulp kappa number after OZ, O(QZ) and OP(QZ) stages reduced by 69.1% 70.6% and 76.5% respectively. The improvement in pulp brightness after OZ, O(QZ) and OP(QZ) stages were obtained 58.3, 60.2 and 69.2% (ISO) respectively. Whereas, reduction in pulp viscosity after OZ, O(QZ) and OP(QZ) stages were found 23.4%, 24.6 and 29.6 respectively. The final bleached pulps were obtained applying OZDEpD, O(QZ)PP and OP(QZ)PP bleaching sequences in order to get 85% (ISO) pulp brightness. The results of ODEpD, OZDEpD, O(QZ)PP and OP(QZ)PP bleaching of pulps showed that pulp brightness, viscosity and post color number (PC number) obtained {85.4%(ISO), 88.6%(ISO), 84.2%(ISO), 87.3%(ISO)}, (690cc/gm, 640cc/gm 612cc/gm, 589cc/gm) and (0.98, 0.58, 0.33, 0.12) respectively.

4.2 Effect of partially and eco- friendly ozone bleaching on pulp characteristics & physical strength properties wheat straw pulp

Table 8 results reveals that unbleached wheat straw pulp with a kappa number 12.6, a intrinsic viscosity of 920 cc/gm and brightness of 32.2% (ISO) bleached with ODEpD, OZDEpD, O(QZ)PP and OP(QZ)PP bleaching sequences. The pulp kappa number after OZ, O(QZ) and OP(QZ) stages reduced by 67.1% 68.6% and 73.5% respectively. The improvement in pulp brightness after OZ, O(QZ) and OP(QZ) stages were obtained 68.2, 69.8 and 75.4% (ISO) respectively. Whereas, reduction in pulp viscosity after OZ, O(QZ) and OP(QZ) stages were found 28.3%, 29.0 and 36.0 respectively. The final bleached pulp were obtained applying OZDEpD, O(QZ)PP and OP(QZ)PP bleaching sequences in order to get 85% (ISO) pulp brightness. The results of ODEpD, OZDEpD, O(QZ)PP and OP(QZ)PP bleaching of pulps showed that pulp brightness, viscosity and post color number (PC number) obtained {83.0%(ISO), 86.7%(ISO), 84.0%(ISO), 85.1%(ISO)}, (577cc/gm, 512cc/gm 563cc/gm, 532cc/gm) and (0.90, 0.67, 0.32, 0.26) respectively.

4.3 Effect of ozone stabilizer (chelant) on pulp characteristics & physical strength properties of ozone treated bagasse pulp

Applications of chelant such as DTPA during ozone bleaching protect the cellulose during ozone bleaching of bagasse pulp. Jacobsen et al (3) reported that ozone react readily with lignin along with carbohydrate present in agro pulps. Table 15 reveals that the addition of DTPA dose @ of 0.5% during ozone bleaching of bagasse pulp the improvement in pulp brightness and pulp viscosity 1.4 unit & 1.7 units and 8.38% & 5.60% in case of O(QZ)PP) & OP(QZ)PP bleaching sequence compared to control samples and act as radical scavenger which is responsible for the major attack on cellulose. The addition of DTPA in TCF bleaching O(QZ)PP) & OP(QZ)PP is also improved tensile index 2.85% & 3.36% and tear index 2.55% & 5.59% of bleached bagasse and wheat straw pulps .

4.4 Effect of ozone stabilizer (chelant) on pulp characteristics & physical strength properties of ozone treated wheat straw pulp

Table 17 reveals that the addition of DTPA dose @ of 0.5% during ozone bleaching of wheat straw pulps the improvement in pulp brightness and pulp viscosity 1.1 unit & 0.9 units and 3.59% & 2.54% in case of O(QZ)PP) & OP(QZ)PP bleaching sequence compared to control samples and act as radical scavenger which is responsible for the major attack on cellulose. The addition of DTPA in TCF bleaching O(QZ)PP) & OP(QZ)PP is also improved tensile index 5.87% & 4.85% and tear index 4.31% & 4.60% of bleached bagasse and wheat straw pulps.

Table 4: Optimization of Kraft and Soda pulping of wheat straw to get desire kappa number

WHEAT STRAW						
S. No.	**Parameters**	**Unit**	**Kraft Pulping**		**Soda Pulping**	
			1	2	1	2
1.	O.D. weight	gm	**100**	100	100	**100**
2.	Sulphidity	%	**20.0**	20.0	-	**-**
3.	Active Alkali charge % (as Na_2O)	%	**11**	13	15	**16**
4.	Unscreened yield	%	**52.2 0**	48.43	52.2	**50.00**
5.	Reject content	%	**0.20**	0.33	0.43	**0.30**
6.	Screened yield	%	**52.00**	48.13	51.87	**49.70**
7.	Kappa number		**12.8**	10.1	17.6	**13.03**
8.	Brightness (ISO)	%	**32.9**	34.38	32.0	**31.50**
9.	Viscosity	cc/gm				**895**

Black Liquor Characteristics						
10.	pH	%	**11.5**	11.7	11.46	**12.1**
11.	Total solids	%,(w/w)	**11.90**	11.30	12.0	**11.0**
12.	Residual active alkali	g/l	**3.23**	2.49	3.16	**3.28**

Constant Cooking Conditions: Ambient to 100^0 C – 30 min, 100^0 C to 160^0 C - 90 min at 160^0 C – 90 and bath ratio – 1:5

Table 5: Large Scale Soda Pulping of Wheat Straw

Wheat Straw soda pulping			
S. No.	**Parameters**	**Unit**	
1.	O.D. weight	gm	**1200**
2.	Active Alkali charge % (as Na_2O)	%	**16**
3.	Unscreened yield	%	**50.8**
4.	Reject content	%	**0.3**
5.	Screened yield	%	**50.5**
6.	Kappa number		**13.11**
7.	Brightness (ISO)	%	**32.16**
8.	Pulp viscosity	cc/gm	**902**
Black Liquor Characteristics			
9.	pH	%	**11.9**
10.	Total solids	%,(w/w)	**12.5**
11.	Residual active alkali	g/l	**3.14**

Constant Cooking Conditions: Ambient to 100^0 C – 30 min, 100^0 C to 160^0 C - 90 min at 160^0 C – 90 and bath ratio – 1:5

Table 6: Optimization of Kraft and Soda pulping of bagasse to get desire kappa number

Bagasse					
S. No.	**Parameters**	**Unit**	**Kraft Pulping**		**Soda Pulping**
			1	**2**	**1**
1.	O.D. weight	gm	**100**	100	100
2.	Sulphidity	%	**20.0**	20.0	-
3.	Active Alkali Charge % (as Na_2O)	%	**14**	15	15
4.	Unscreened yield	%	**55.1**	54.6	60.1
5.	Reject content	%	**0.40**	0.30	4.2
6.	Screened yield	%	**54.60**	54.30	55.6
7.	Kappa number		**14.3**	11.21	26.1
8.	Brightness (% ISO)	%	**29.1**	30.32	26.0
9.	Viscosity	cc/gm	**1032**		
Black Liquor Characteristics					
10.	pH	%	**12.12**	12.2	11. 1
11.	Total Solids	%(w/w)	**12.0**	11.39	9.96
12.	Residual active alkali	g/l	**2.82**	3.15	2.03

Constant Cooking Conditions: Ambient to 100^0 C – 30 min, 100^0 C to 160^0 C - 90 min at 160^0 C – 90 and bath ratio – 1:4.5

Table 7: Large Scale Kraft Pulping of Bagasse

Bagasse Kraft Pulping			
S. No.	**Parameters**	Unit	
1.	O.D. weight	gm	**1000**
2.	Alkali charge as NaOH	%	**14**

3.	Unscreened yield	%	55.30
4.	Reject Content	%	0.2
5.	Screened yield	%	55.1
6.	Kappa Number		13.6
7.	Brightness (ISO)	%	30.1
8.	Pulp viscosity	cc/gm	1013
Black Liquor Characteristics			
9.	pH	%	12.8
10.	Total Solids	%(w/w)	11.7
11.	Reasidual active alkali	g/l	3.34

Table 8: Result of OP stage of unbleached bagasse and wheat straw pulps

S.No.	Analysis	Unit	Bagasse			Wheat straw		
	Before ODL							
1.	Kappa number		13.6			12.6		
2.	Pulp brightness	% (ISO)	30.1			32.16		
3.	Pulp viscosity	cm^3/g	1013			902		
4.	After ODL							
	Peroxide charge	%	1	2	3	1	2	3
5.	Kappa number		6.80	4.88	4.18	6.21	4.52	4.17
6.	Pulp brightness	% (ISO)	43.2	49.3	53.8	37.9	43.02	48.39
7.	Pulp viscosity	cc/gm						
8.	Pulp yield	%	97.29	96.12	95.25	97.75	95.97	94.85

Constant Conditions: Pulp consistency - 10%, Oxygen pressure -5kg/cm2, Temperature - .90 ±20 C and reaction time – 60 min

Table 9: Results of ECF, Light ECF and eco-friendly ozone bleaching sequences of bagasse pulp

S.No.	Parameters	Units	Bagasse pulp			
	Bleaching Sequence	%	ODEpD	OZDEpD	O(QZ)PP	OP(QZ)PP
1.	Unbleached pulp Kappa number		13.0	13.0	13.0	13.0
2.	Kappa number after ODL		6.8	6.8	6.8	6.8
3.	Brightness after ODL	%(ISO)	43.2	45.1	45.1	53.1
4.	Viscosity after ODL	cc/gm	854	854	854	790
Chelation stage (Q) stage						
5.	DTPA added		-	-	0.5	0.5
6.	MgSo4	%	-	-	0.05	0.05
7.	Sodium silicate	%	-	-	0.5	0.5
8.	Brightness	%(ISO)	-		44.3	54.0
Z stage						
9.	Ozone dosage	%		0.50	0.50	0.50
10.	Kappa number after Z stage			4.2	4.0	3.2
11.	Brightness after Z stage			58.3	60.2	69.2
12.	Viscosity after Z stage			776	764	713
D_0 stage						

13.	Cl_2 factor applied	%	0.22	0.20		
14.	ClO_2 applied as D	%	1.61	0.84		
15.	Final pH		2.2	2.3		
Extraction stage E_P/P_1						
16.	Alkali applied	%	1.5	1.5	1.0	1.0
17.	Peroxide applied	%	1.0	1.0	2.5	2.5
18.	Pulp brightness	%, (ISO)	70.1	81.0	71.0	80.3
19.	Pulp viscosity	cc/gm	757	656	687	626
D_1 Stage/ P_2 stage						
20.	Dioxide applied as D	%	1.0	0.5		
21.	Residual ClO_2	ppm	45	32		
22.	Pulp brightness, ISO	%	85.4	88.6		
23.	Pulp viscosity	cc/gm	690	640		
Final P_2 stage						
24.	Peroxide applied	%	-	-	1.5	1.5
25.	Alkali applied as buffer	%	-	-	1.0	1.0
26.	Pulp brightness	%, (ISO)	-	-	84.2	87.3
27.	Pulp viscosity	cc/gm	-	-	612	589
28.	PC number	-	0.98	0.58	0.33	0.12

Table 10: Results of ECF, Light ECF and eco-friendly ozone bleaching sequences of wheat straw pulp

S. No.	Parameters	Units	Wheat straw pulp			
	Bleaching Sequence	%	**ODEpD**	**OZDEpD**	**O(QZ)PP**	**OP(QZ)PP**
1.	Unbleached pulp Kappa		12.6	12.6	12.6	12.6
2.	Kappa number after ODL		6.5	6.5	6.5	5.7
3.	Brightness after ODL	%(ISO)	41.2	41.2	41.2	48.2
4.	Viscosity after ODL	cc/gm	765	765	765	695
Chelation stage (Q) stage						
5.	DTPA added		-	-	0.5	0.5
6.	MgSo4	%	-	-	0.05	0.05
7.	Sodium silicate	%	-	-	0.5	0.5
8.	Brightness	%(ISO)	-		42.3	49.4
Z stage						
9.	Ozone dosage	%		0.50	0.50	0.50
10.	Kappa number after Z stage			4.0	3.8	3.1
11.	Brightness after Z stage			52.4	53.5	62.0
12.	Viscosity after Z stage			660	653	589
D_0 stage						
13.	Cl_2 factor applied	%	0.22	0.20		
14.	ClO_2 applied as D	%	1.43	0.80		
15.	Final pH		2.3	2.4		
Extraction stage E_P/P_1						
16.	Alkali applied	%	1.5	1.5	1.0	1.0
17.	Peroxide applied	%	1.0	1.0	2.5	2.5
18.	Pulp brightness	%, (ISO)	70.0	75.0	71.2	73.0
19.	Pulp viscosity	cc/gm	634	586	576	512
D_1 Stage						
20.	Dioxide applied as D	%	1.0	0.5		
21.	Residual ClO_2	ppm	43	34		
22.	Pulp brightness, ISO	%	83.0	86.7		

23.	Pulp viscosity	cc/gm	597	512		
Final P_2 stage						
24.	Peroxide applied	%	-	-	1.5	1.5
25.	Alkali applied as buffer	%	-	-	1.0	1.0
26.	Pulp brightness	%,(ISO)	-	-	84.0	85.1
27.	Pulp viscosity	cc/gm	-	-	563	532
28.	PC number	-	0.90	0.67	0.32	0.26

Table 11: Results of TCF bagasse pulp using with and without ozone stabilizer chemical

S. No.	Parameters	Units	Bagasse pulp			
			O(QZ)PP		OP(QZ)PP	
	Bleaching Sequence	%	Control	Z Stabilizer	Control	Z Stabilizer
1.	Unbleached pulp Kappa number		13.0		13.0	
2.	Kappa number after ODL		6.8		6.8	
3.	Brightness after ODL	%(ISO)	45.1		53.1	
4.	Viscosity after ODL	cc/gm	854		790	
Z stage						
5.	Ozone dosage	%	0.50	0.50	0.50	0.50
6.	DTPA	%	-	0.50	-	0.50
7.	Kappa number after Z-stage		4.1	3.8	3.4	3.0
8.	Brightness after Z stage		60.5	62.8	69.8	70.9
9.	Viscosity after Z stage		764	787	713	744
Extraction stage E_P/P_1						
10.	Alkali applied	%	1.0	1.0	1.0	1.0
11.	Peroxide applied	%	2.5	2.5	2.5	2.5
12.	Pulp brightness	%, (ISO)	71.0	72.9	71.0	73.1
13.	Pulp viscosity	cc/gm	687	732	687	726
Final P_2 stage						
14.	Peroxide applied	%	1.5	1.5	1.5	1.5
15.	Alkali applied as buffer	%	1.0	1.0	1.0	1.0
16.	Pulp brightness	%,(ISO)	84.2	85.6	87.3	87.3
17.	Pulp viscosity	cc/gm	612	668	589	622
18.	PC number	-	0.33	0.19	0.12	0.04

Table 12: Results of TCF wheat straw pulp using with and without ozone stabilizer

chemical

S. No.	Parameters	Units	Wheat straw pulp			
			O(QZ)PP		OP(QZ)PP	
	Bleaching Sequence	%	Control	Z Stabilizer	Control	Z Stabilizer
1.	Unbleached pulp Kappa number		12.6	12.6	12.6	12.6
2.	Kappa number after ODL		6.5	6.5	5.7	5.7
3.	Brightness after ODL	%(ISO)	41.2	41.2	48.2	48.2
4.	Viscosity after ODL	cc/gm	765	765	695	695

Chelation stage (Q) stage						
5.	DTPA added		0.5	0.5	0.5	0.5
6.	MgSo4	%	0.05	0.05	0.05	0.05
7.	Sodium silicate	%	0.5	0.5	0.5	0.5
8.	Brightness	%(ISO)	42.3	42.3	49.4	49.4
Z stage						
9.	Ozone dosage	%	0.50	0.50	0.50	0.50
10.	DTPA	%	-	0.50	-	0.50
11.	Kappa number after Z stage		3.9	3.6	3.1	2.9
12.	Brightness after Z stage		53.5	54.6	62.0	63.5
13.	Viscosity after Z stage		653	680	589	612
Peroxide stage P_1						
14.	Alkali applied	%	1.5	1.5	1.5	1.5
15.	Peroxide applied	%	1.0	1.0	1.0	1.0
16.	Pulp brightness	%,(ISO)	70.0	72.0	75.0	76.4
17.	Pulp viscosity	cc/gm	634	647	586	601
Final P_2 stage						
18.	Peroxide applied	%	1.5	1.5	1.5	1.5
19.	Alkali applied as buffer	%	1.0	1.0	1.0	1.0
20.	Pulp brightness	%,(ISO)	84.0	85.1	85.1	86.0
21.	Pulp viscosity	cc/gm	612	634	578	592
22.	PC number	-	0.32	0.27	0.26	0.20

Table 13: optimized bleaching conditions for different bleaching sequence

Parameters	O stage	OP stage	Q stage	Z stage	D1 stage	Ep stage	P1 and P2 stage	D2 stage
Consistency, %	10	10	5	8	5	10	10	10
Reaction time, min	90	90	60	15	60	90	90	180
Reaction temp, 0C	90	120	50	40	80	70	90	80
End pH	11-12	11-12	5-6	2-3	2-3	11-12	10-11	3-4

Table 14: Results of ECF and Light ECF/TCF bleaching sequences of bagasse pulp

Parameters	Unit	ODEpD	OZDEpD	O(QZ)PP	OP(QZ)PP
Final pulp brightness	,%(ISO)	85.4	88.6	84.2	87.3
Bleached pulp viscosity,	cc/gm	690	640	612	589
PC number		0.98	0.58	0.33	0.12
Tear index	$mN.m^2/g$	6.34	6.12	5.87	5.90
Tensile index	Nm/g	56.9	55.0	52.6	53.6

Table 15: Results of ECF and Light ECF/TCF bleaching sequences of bagasse

Parameters	Unit	Control	C. Stabilzer	Control	C. Stabilzer
		O(QZ)PP	O(QZ)PP	OP(QZ)PP	OP(QZ)PP

Final pulp brightness	%(ISO)	84.2	85.6	87.3	89.0
Bleached pulp viscosity	cc/gm	612	668	589	622
PC number		0.33	0.19	0.12	0.04
Tear index, $mN.m^2/g$	$mN.m^2/g$	5.87	6.02	5.90	6.23
Tensile index	Nm/g	52.6	54.1	53.6	55.4

Table16: Comparison of bleached pulp characteristics and physical strength properties different ECF and Light ECF/TCF bleaching sequences of Wheat straw pulp

Parameters	Unit	ODEpD	OZDEpD	O(QZ)PP	OP(QZ)PP
Final pulp brightness	%(ISO)	83.0	86.7	84.0	85.1
Bleached pulp viscosity,	cc/gm	597	512	612	589
PC number		0.90	0.67	0.32	0.26
Tear index	$mN.m^2/g$	5.17	4.87	4.63	5.0
Tensile index	Nm/g	52.7	51.0	49.4	51.5

Table 17: Comparison of control and carbohydrate stabilizer bleached pulp characteristics and physical strength properties of TCF bleaching sequences of wheat straw pulps

Parameters	Unit	Control	C. Stabilzer	Control	C. Stabilzer
		O(QZ)PP	O(QZ)PP	OP(QZ)PP	OP(QZ)PP
Final pulp brightness	%(ISO)	84.0	85.1	85.1	86.0
Bleached pulp viscosity	cc/gm	612	634	589	592
PC number		0.32	0.27	0.26	0.20
Tear index	$mN.m^2/g$	4.63	4.83	5.0	5.23
Tensile index	Nm/g	49.4	52.3	51.5	54.0

4.5 Effluent load of ECF, Light ECF and Eco friendly ozone Bleaching of bagasse and wheat straw pulp

The extent of pollution and toxicity depends upon the raw material used, pulping method, and pulp bleaching process adapted by the pulp and paper mills. For example, the pollution load from hardwood is lower than softwood. On the other hand, the spent liquor generated from pulping of non wood fiber has a high silica content. Volumes of wastewater discharged may vary from near zero to 400 m3 per ton of pulp depending on the raw material used, manufacturing process, and size of the mill .Thus, the variability of effluent characteristics and volume from one mill to another emphasizes the requirement for a variety of pollution prevention and treatment technologies, tailored for a specific industry.

The use of elemental chlorine in pulp bleaching has been gradually discontinued in several countries to prevent the toxic effects of chlorinated organic compounds in receiving waters and to meet regulatory requirements. Most nations have imposed stringent regulatory limits on AOX, ranging from 0.3 to 2.0 kg/ton of pulp. Cleaner bleaching methods have been developed by industries based on elemental chlorine free (ECF), total chlorine free (TCF), microbial systems (bio-bleaching), extended delignification, and methods for monitoring and improved control of bleaching operations. Each of these approaches is discussed in the following subsections. Elemental Chlorine Free (ECF) and Total Chlorine Free (TCF) Bleaching Elemental chlorine has been replaced by chlorine dioxide and hypochlorite in the ECF bleach sequence, while oxygen, ozone, caustic soda, and hydrogen peroxide have been advocated for TCF bleaching of softwood and hardwood Kraft pulps. Benefits include significant reduction in the formation of chlorinated organic compounds or their elimination and lower ecological impacts. Two

Finnish mills eliminated elemental chlorine from the bleach sequence and substituted chlorine dioxide, thereby sharply reducing the concentration of chlorinated cymenes. In another Finnish example, levels of chlorinated poly aromatic hydrocarbons in mill wastes were substantially reduced during production of bleached birch Kraft pulp without the use of elemental chlorine as

Compared to pine pulp bleached with elemental chlorine. Research has also been conducted on the optimal usage of agents such as ozone and hydrogen peroxide. However, alternatives such as ozonation, oxygenation, and peroxidation are not economically viable for medium- or small-capacity mills due to higher capital investments and plant operation costs.

4.6 Effluent generated during light ECF and TCF bleaching sequences

The combined effluent generated in ECF and TCF bagasse and wheat straw pulp bleaching sequences i.e. ODEpD, OZDEpD, O(QZ)PP and OP (QZ)PP are depicted in tables 18 & 19. The effluent parameters i.e. COD in case of OP (QZ)PP sequence are high as compared to other sequences because due to dissolution of hemicelluloses from the pulp. It is clear that if TCF bleaching filtrate may recycled back in the system and the filtrate from bleach plant can be minimized greatly

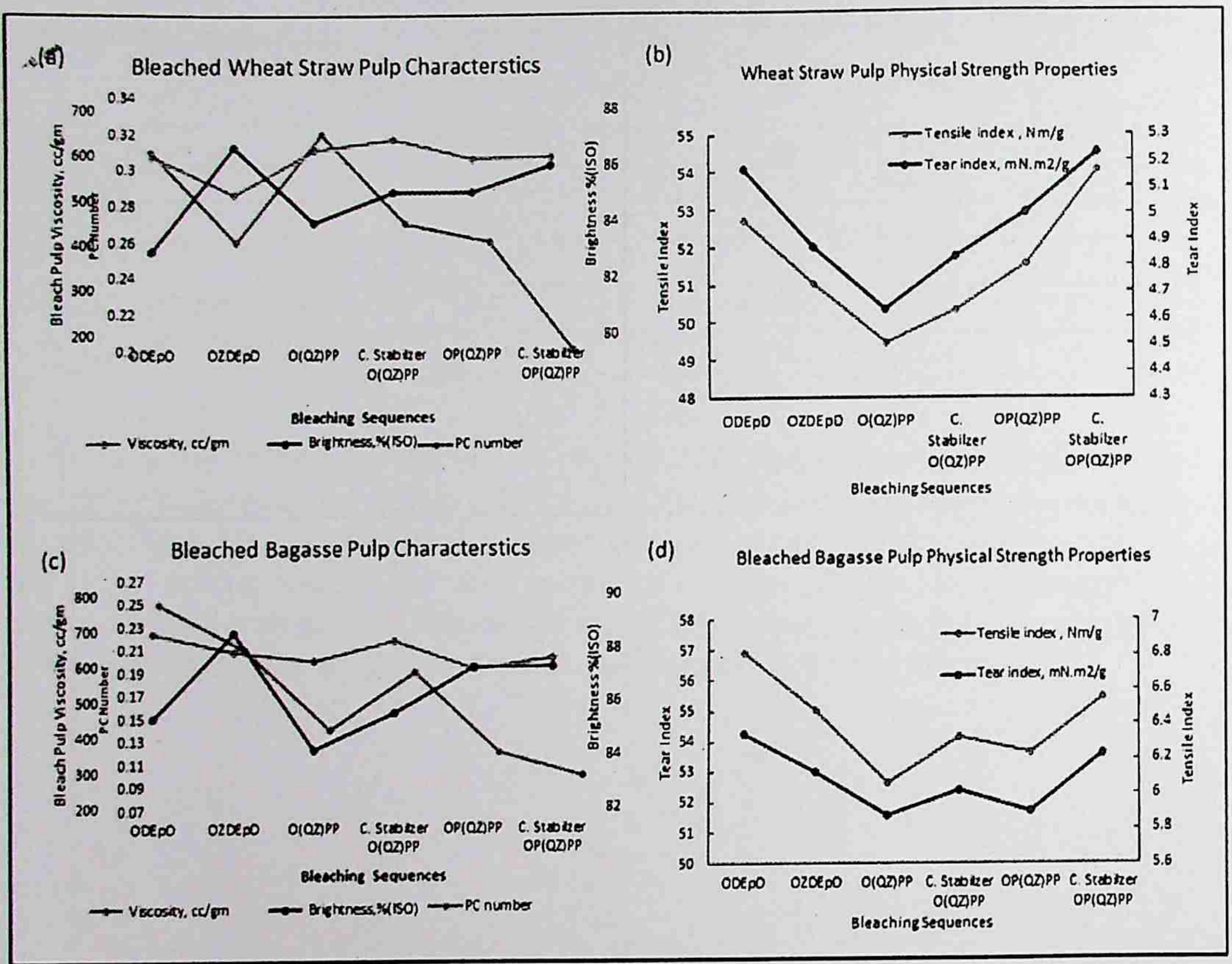


Figure 4:- Final bleached pulp characteristics i.e, (a) Viscosity (cc/gm), Brightness %(ISO), PC number of bagasse (b) tensile index (Nm/g), tear index mN.m^2/g of bagasse (c) Viscosity (cc/gm), Brightness %(ISO), PC number of wheat straw (d) tensile index (Nm/g), tear index mN.m^2/g of wheat straw at different bleaching sequences.

Table 18. Characteristics of Effluent generated during bagasse pulp bleaching

Bleaching Sequences	COD, mg/l	TSS, mg/l	BOD, mg/l	TDS, mg/l	Color, ptc number
ODEpD	803	195	586	3306	31
OZDEpD	1045	174	780	3421	24
O(QZ)PP	987	215	656	2860	18
OP(QZ)PP	1176	226	813	2754	21
O(QZ)PP (C.Stabilizer)	910	210	587	2741	14
OP(QZ)PP (C. Stabilzer)	1036	216	787	2710	10

Table 19. Characteristics of Effluent generated during wheat straw pulp bleaching

Bleaching Sequences	COD, mg/l	TSS, mg/l	BOD, mg/l	TDS, mg/l	Color, ptc number
ODEpD	768	187	547	3126	35
OZDEpD	1112	217	812	3478	26
O(QZ)PP	958	221	689	2932	17
OP(QZ)PP	1216	234	875	3245	19
O(QZ)PP (C. Stabilizer)	887	203	506	3031	15
OP(QZ)PP (C. Stabilizer)	1145	210	832	3178	10

The combined effluent generated in ECF and TCF bagasse and wheat straw pulp bleaching sequences i.e. ODEpD, OZDEpD, O(QZ)PP and OP (QZ)PP are depicted in tables 18 & 19. The effluent parameters i.e. COD in case of OP (QZ)PP sequence are high as compared to other sequences because due to dissolution of hemicelluloses from the pulp. It is clear that if TCF bleaching filtrate may recycled back in the system and the filtrate from bleach plant can be minimized greatly.

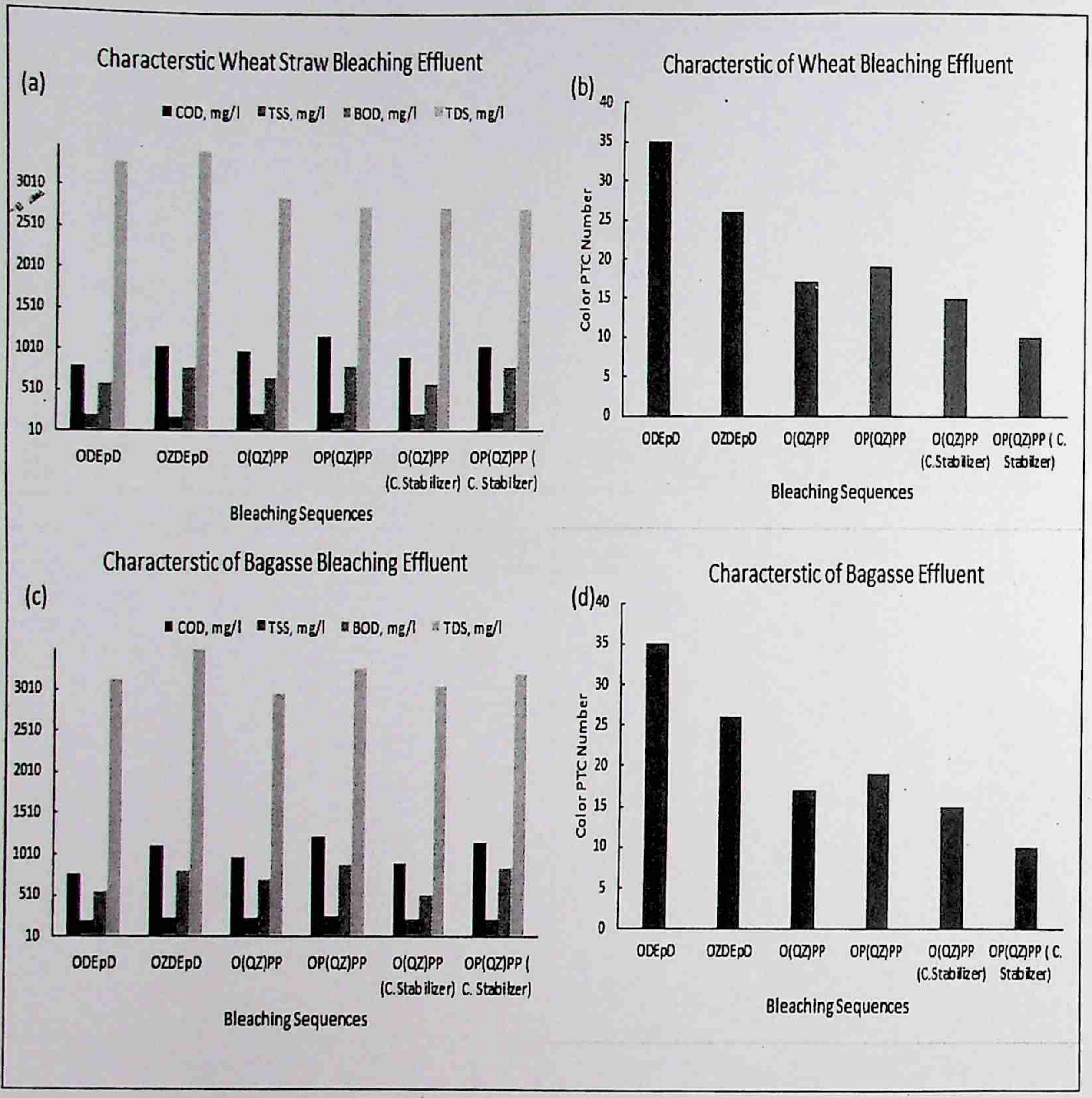


Fig 5: Effluent characteristics (a) COD, TSS, BOD and TDS mg/l of wheat straw (b) color load of wheat straw (c) COD, TSS, BOD and TDS mg/l of bagasse (d) color load of bagasse in bleaching effluent different bleaching sequences.

5. Development of Design of Ozone Reactor

Figure 6. Laboratory Quantum mixture for oxygen bleaching of pulp

5.1 Details of horizontal laboratory scale ozone reactor quantum mixture

Ozone treatment of pulp was carried out in quantum mixture. 250g OD pulp sample was taken for ozone experiments. Before ozone treatment pulp was acidified with sulphuric acid to pH 2.5. Pulp pad of 12% consistency was prepared. The reactor bowl is of SS 316(rust free steel) and can bear both strong acid and alkali conditions. Conditions of Z treatment are as cited below. Dose of ozone were applied after calculating demand based on chlorine equivalent. The flow of ozone is adjusted according to the demand of ozone.

Consistency,%	1,2,3,45
Temperature, °C	Ambient
pH	2.5
Reaction Time , min.	2.5
Pulp mixer speed, RPM	120,240,600
Retention time, min.	10

Laboratory quantum mixture is vertical with 2 liter volume bowl with mixing shaft. In mills for ozone treated pulp sending to fiber line for further bleaching experiment should be horizontal. In quantum mixture mixing could be done up to 1200 RPM by operating consistency from lower to medium i.e, 5-10 % for good performance. Ozone insertion point at the below of mixture. Temperature could be maintained up to 50°C but no need of high temperature, experiments conducted at ambient temperature.

5.2 Details of the study on effect of variables on ozone and lignin reaction i.e. efficacy.

5.2.1 Pulp consistency

The ozone containing gas can be continuously introduced by flowing the gas through both side of the reactor to contact the cellulosic fibrous material. Preferably, this material is a pulp having a pH of about 1.5 to 2.5 and a consistency of about 15 to 20%.

Early work showed high consistency produced the strongest pulp. Later results show at low and medium consistency. Lindholm and Wannerstrom conclude that selectivity of bleaching was better at low consistency than at high consistency, particularly when bleaching to low kappa number levels. Low consistency has its own disadvantages they are large water demand, large effluent volume, and mixing volume. In medium consistency gas to pulp ratio must be small enough to be adequately mixed yet the ozone concentration must be high has been found to be highly effective. Liebergott and Sun found kappa number of the pulp decreased as the consistency was lowered from 25-53%. The higher the pulp consistency, lower the amount of ozone required per unit of kappa kappa number drop. The viscosity of soft wood and hardwood kraft pulps did not appear to be affected by the changes up to 46% consistency. Lindholm also give mechanical pulp strength property can be achieve better at low consistency compare to high consistency ozone in ozone stage.

5.2.2 Pulp mixing RPM

Increasing mixing intensity improve viscosity protection and delignification when adequate reaction times were used in medium consistency bleaching. There is higher ozone consumption at higher mixer speeds when ozonating at medium consistency. During ozone bleaching of agro pulps rotational speeds of the paddles in ozone reactor means less than about 50 rpm. More specifically, the conveying means may comprise a rotatable shaft extending longitudinally through the shell in a helical half-pitch pattern. The paddles may be spaced apart in the longitudinal direction to provide an un swept distance between paddles.

5.2.3 Charge and pH

A pH between 2 and 3 is optimal for pulp ozonation. Delignification is improved at low ph and the strong acidity does not contribute to substantial losses of viscosity. Viscosity loss is minimal because of three factors. Decomposition reactions that produce radical are inhibited. Metal that promote ozone decomposition may be removed in acidic condition and primary ozone lignin reaction may be favored. The dependency of delignification on Ph has been found to be more complicated when pulps have a higher residual lignin content.

5.2.4 Concentration

In general concentration below 10% have been used for the safety concern and limitation on ozone generator when increasing the concentration up to 2-3% by weight, lower concentration improved viscosity using high consistency condition. Than 10% concentration found more selective than 2-3% with high consistency. High concentration reduces the time for delignification and more selective at medium consistency at low charge of ozone.

5.2.5 Time

This allows for extremely short extraction stages of 5-10 minutes in the case of hardwood pulp, while longer retention time may bring benefits for softwood pulp bleaching. Acidified cellulosic agro fibrous material at high consistency (e.g., 15-20%) can be delignified by fluffing the material so that it is loose with a high surface area to volume ratio, adding ozone containing gas to the material, with the amount of ozone being effective to delignify the material, and maintaining the material in contact with the ozone containing gas for at least a few seconds up to a few minutes i.e 3 min while tumbling the material to keep the fluffed material loose and homogeneous with a high surface area to volume ratio and well mixed with the ozone containing gas. The latter step is preferably conducted by simultaneously tumbling the material and continuously conveying it in a first direction so that the retention time is about 1-3 minutes.

5.3 Results of detail study on effect of variables on ozone and lignin reaction i.e. efficacy.

Table 1: Effect of mixing (120, 240 and 600) at 1% consistency on pulp characteristics:

S. No.	Parameters	Unit	Control	Exp1	Exp2	Exp3
1.	RPM		-	120	240	600
2.	Pulp brightness	ISO (%)	54.5	54.2	54.3	54.2
	Gain/drop	unit	0	-0.3	-0.2	-0.3
3.	Kappa number		9.6	9.7	9.5	9.7
	Gain/drop	**unit**	**0**	**-0.2**	+ 0.1	**-0.2**
4.	Pulp viscosity	cc/g	808	780	792	780
	Gain/drop	**unit**	**0**	**-28**	**-16**	**-28**
5.	ODL pulp freeness	ml, CSF	480	462	466	462
	Gain/drop	**unit**	**0**	**-18**	**-14**	**-18**
6.	Tear Index	mN.m²/g	6.2	6.0	6.1	6.0
	Gain/drop	**unit**	**0**	**-0.2**	**0**	**-0.2**
7.	Tensile Index	Nm/g	39.2	40.4	40.0	40.4
	Gain/drop		**0**	**+1.2**	**+0.8**	**+1.2**

Condition: Pulp Consistency 1%, Time 2 min. and Temperature °C -Ambient

Table. 2: Effect of mixing (120, 240 and 600) at 2% consistency on pulp characteristics:

Sr. No.	Parameters	Unit	Control	Exp1	Exp2	Exp3
1.	RPM		-	120	240	600

2.	Pulp brightness	ISO (%)	54.5	53.7	54.0	54.1
	Gain/drop	unit	0	-0.8	-0.5	-0.4
3.	Kappa number		9.6	9.5	9.3	9.0
	Gain/drop	**unit**	**0**	**+ 0.1**	+0.3	**+0.6**
4.	Pulp viscosity	cc/g	808	781	776	763
	Gain/drop	**unit**	**0**	**-27**	**-32**	**-35**
5.	ODL pulp freeness	ml, CSF	480	465	458	454
	Gain/drop	**unit**	**0**	**-15**	**-22**	**-26**
6.	Tear Index	mN.m²/g	6.2	6.1	5.9	5.8
	Gain/drop	**unit**	**0**	**-0.1**	**-0.3**	**-0.4**
7.	Tensile Index	Nm/g	39.2	40.2	41.0	41.6
	Gain/drop		**0**	**+1.0**	**+1.8**	**+2.4**

Condition: Pulp Consistency 2%, Time 2 min. and Temperature °C -Ambient

Table 3: Effect of mixing (120, 240 and 600) at 3% consistency on pulp characteristics:

Sr. No.	Parameters	Unit	Control	Exp1	Exp2	Exp3
1.	RPM		-	120	240	600
2.	Pulp brightness	ISO (%)	54.5	53.5	53.7	54.2
	Gain/drop	unit	0	-1.0	-0.8	-0.3
3.	Kappa number		9.6	9.5	9.4	9.3
	Gain/drop	**unit**	**0**	+ 0.1	+0.2	**+0.3**
4.	Pulp viscosity	cc/g	808	776	764	751
	Gain/drop	**unit**	**0**	**-32**	**-34**	**-57**
5.	ODL pulp freeness	ml, CSF	480	461	456	450
	Gain/drop	**unit**	**0**	**-19**	**-24**	**-30**
6.	Tear Index	mN.m²/g	6.2	5.9	5.8	5.7
	Gain/drop	**unit**	**0**	**-0.3**	**-0.4**	**-0.5**
7.	Tensile Index	Nm/g	39.2	40.9	41.5	42.3
	Gain/drop		**0**	**+1.7**	**+2.3**	**+3.1**

Condition: Pulp Consistency 3%, Time 2 min. and Temperature °C -Ambient

Table 4: Effect of mixing (120, 240 and 600) at 4% consistency on pulp characteristics:

Sr. No.	Parameters	Unit	Control	Exp1	Exp2	Exp3
1.	RPM		-	120	240	600
2.	Pulp brightness	ISO (%)	54.5	54.1	54.2	54.0
	Gain/drop	unit	0	-0.4	-0.3	-0.5
3.	Kappa number		9.6	9.5	9.6	9.3
	Gain/drop	**unit**	**0**	+ 0.1	0	**+0.3**
4.	Pulp viscosity	cc/g	808	764	753	744
	Gain/drop	**unit**	**0**	**-32**	**-55**	**-64**
5.	ODL pulp freeness	ml, CSF	480	459	452	448
	Gain/drop	**unit**	**0**	**-21**	**-28**	**-32**
6.	Tear Index	mN.m²/g	6.2	5.7	5.7	5.5
	Gain/drop	**unit**	**0**	**-0.5**	**-0.5**	**-0.7**
7.	Tensile Index	Nm/g	39.2	41.0	42.0	42.3
	Gain/drop		**0**	**+1.9**	**+2.8**	**+3.1**

Condition: Pulp Consistency 4%, Time 2 min. and Temperature °C -Ambient

Table 5: Effect of mixing (120, 240 and 600) at 5% consistency on pulp characteristics:

Sr. No.	Parameters	Unit	Control	Exp1	Exp2	Exp3
1.	RPM		-	120	240	600
2.	Pulp brightness	ISO (%)	54.5	53.7	54.0	53.9
	Gain/drop	unit	0	-0.8	-0.5	-0.6
3.	Kappa number		9.6	9.3	9.1	8.8
	Gain/drop	**unit**	**0**	+ 0.3	+0.5	**+0.8**
4.	Pulp viscosity	cc/g	808	760	749	738
	Gain/drop	**unit**	**0**	**-48**	**-59**	**-70**
5.	ODL pulp freeness	ml, CSF	480	458	450	445
	Gain/drop	**unit**	**0**	**-22**	**-30**	**-35**
6.	Tear Index	mN.m²/g	6.2	5.7	5.5	5.2
	Gain/drop	**unit**	**0**	**-0.5**	**-0.7**	**-1.0**
7.	Tensile Index	Nm/g	39.2	42.1	42.7	43.1
	Gain/drop		**0**	**+3.1**	**+3.5**	**+4.1**

Condition: Pulp Consistency 5%, Time 2 min. and Temperature °C -Ambient

Inferences:

1. There is marginally drop in pulp viscosity and tear index and also slight enhancement in tensile index.
2. Drop in pulp freeness has also been observed.
3. This pattern is follows in case of all consistencies from 1-5.

5.4 Details survey on design of pilot or mill scale reactor and preparation of reactor drawing before initiation of fabrication process for pilot scale reactor

The detailed survey on design of pilot scale ozone reactor carried out. A number of patents on net available with design and most of them are horizontal type reactor. The pressurized horizontal reactor available with paddle type ozone mixing system was selected for design preparation. In initial phase it was decided the design preparation from instrument design expert.

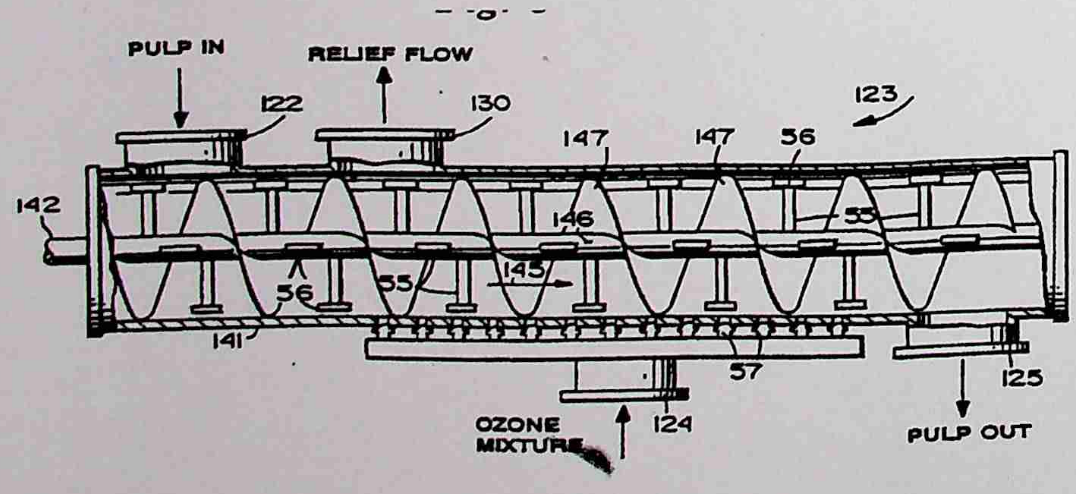


Figure 7:- Design of ozone reactor

Based on the literature and inputs from various design experts the ozone reactor design was prepared with following specifications

1. Size of reactor- 15 lit
2. The pulp weight adjustable ~5 kg
3. pH range acid to alkaline 2-14
4. Pressure range 1-2 kg

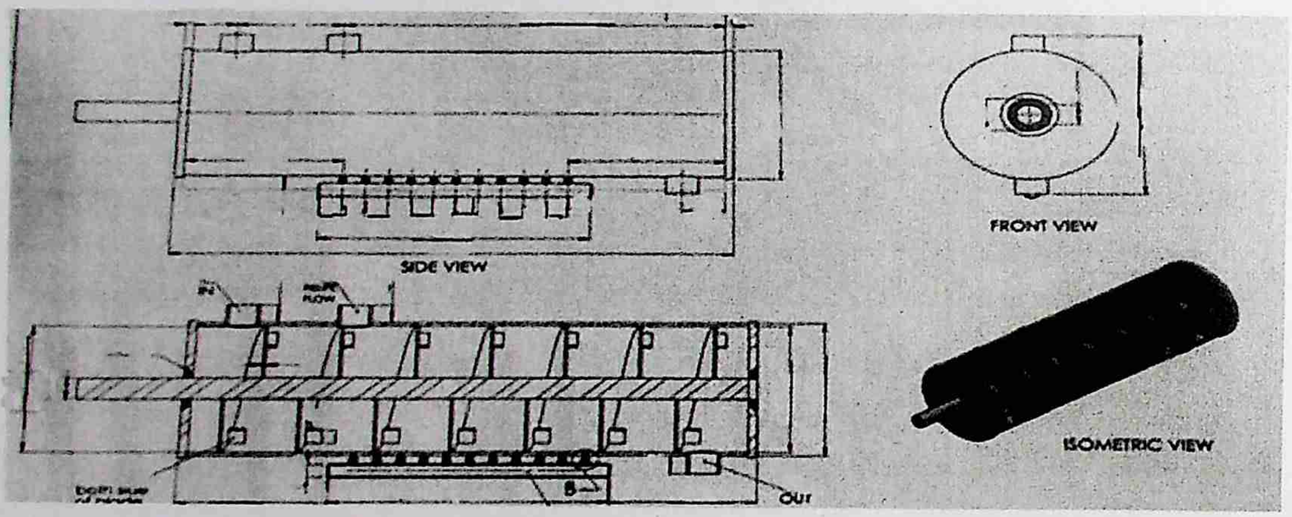
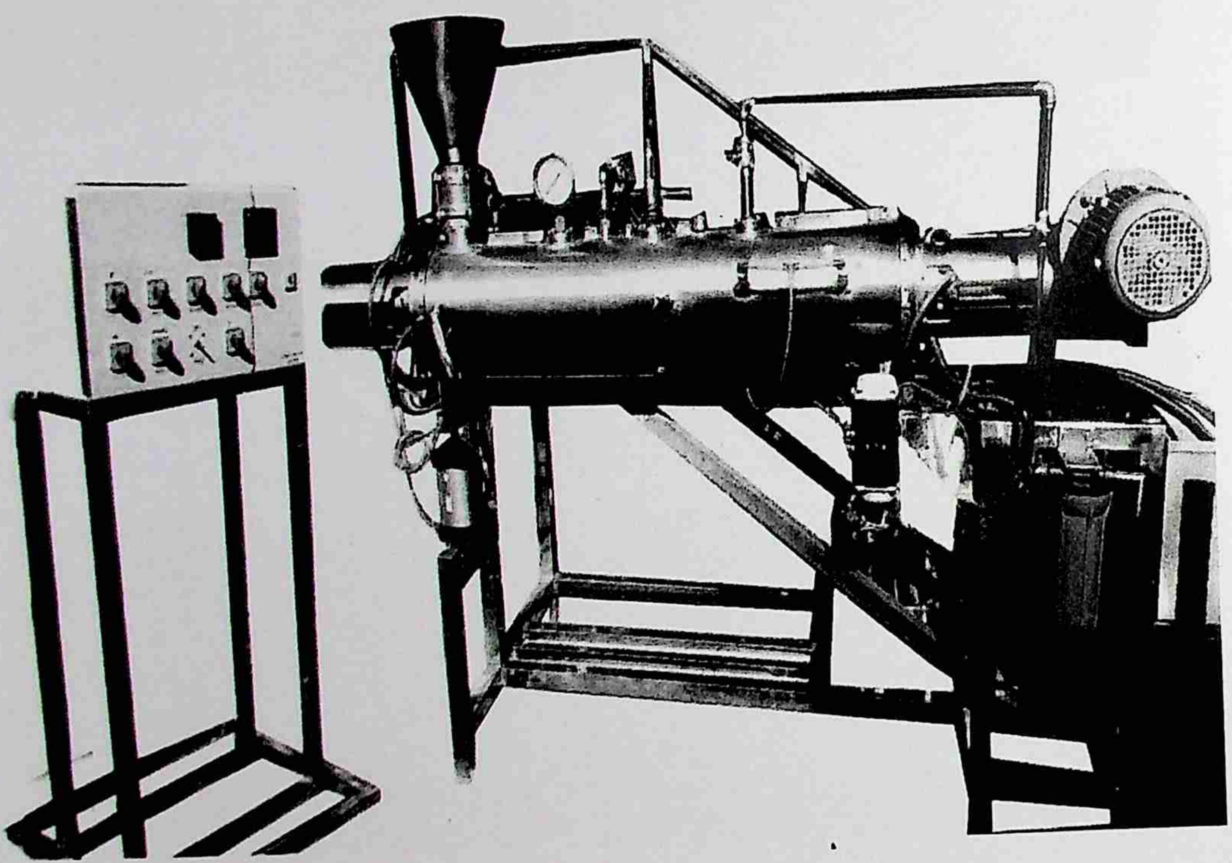
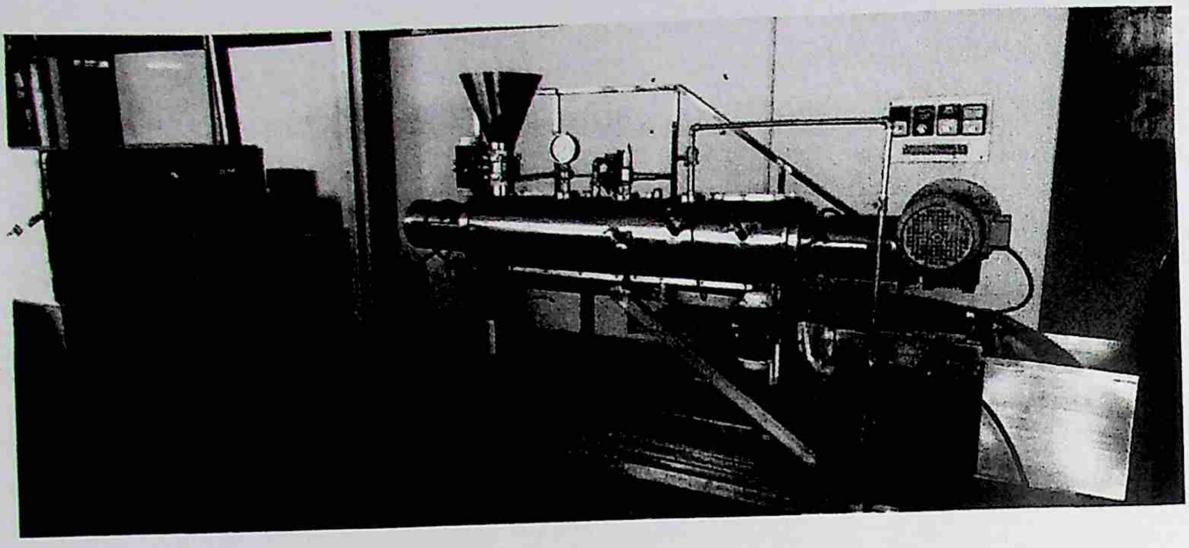


Figure 8: Drawing layout of ozone reactor

6. Integration of Pilot Scale Ozone Reactor





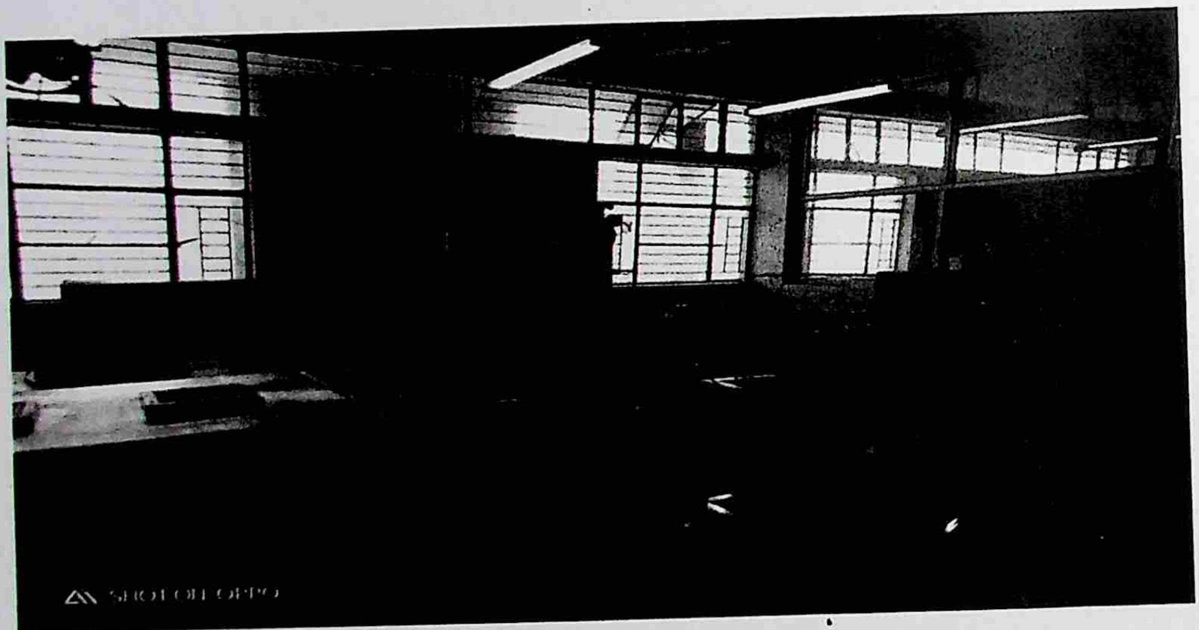


Figure 9: Pilot plant scale ozone facility at CPPRI

6.1 Integration of Ozone Generator

6.1.1 Ozone Generator

The Ozone Generator is a self-standing panel which will have all the ozone generation components along with protection, interlocks to control & operate complete Ozonation system. The ozone generator will be interlocked with all the associated accessories as mentioned in the subsequent portion with the help of Control logic.

- Ozonation Tank

Ozone production on commercial scale is carried out by Corona Discharge technique. Typical feed gas for generation of Ozone is either dry Air or Oxygen. The feed gas is passed through a high voltage discharge in a group of Ozone cells, where the cells are arranged in parallel, series or in combination. The formation of Ozone involves a reaction between an Oxygen atom and an Oxygen molecule and following reactions takes place. (O_2 = O+O O+O_2 = O_3 3O_2 = 2O_3, H = 68 K Cal) During formation of Ozone, only a part of Oxygen gets converted. The percentage of Oxygen getting converted into Ozone depends on several factors and these are: - Percentage of oxygen in Feed Gas - Intensity of Corona discharge - Temperature of Reaction - Rate of flow of Feed Gas - Pressure of Feed Gas. The type of Feed Gas and Oxygen Concentration plays an important role .

For production of lower concentration Ozone, dry air or air with higher percentage of oxygen (more than 20%) is used as a feed gas. Production of Ozone with such feed gas is carried out where a low Ozone concentration (3-4 % wt%) is adequate or desirable for a specific application. It is necessary to completely dry the feed gas for proper operation and long life of Ozone Generator. For removal of moisture a PSA (Pressure Swing Absorption) based dryer or any specific air drying technique is used to obtain dryness of air to the tune of –60oC Dew Point.

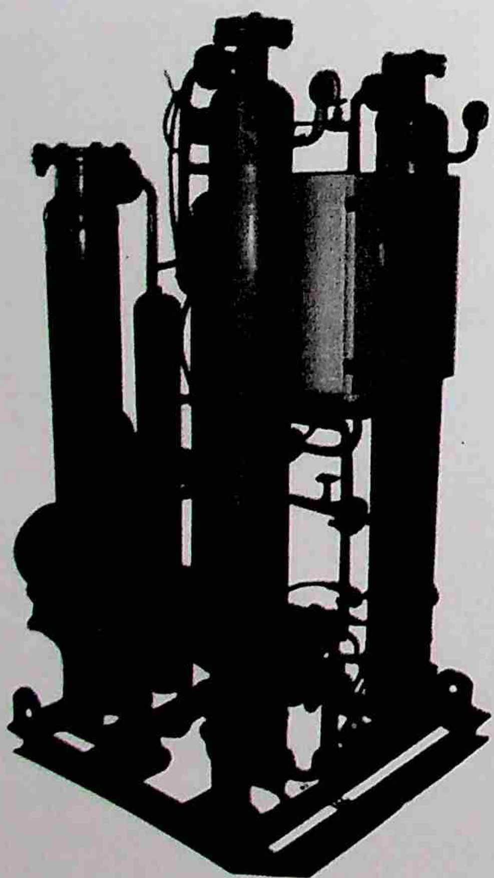
A typical air preparation system for an Ozone generator consists of an

- Air Compressor,
- Air receiver,
- a Double column PSA drier,
- Buffer tank,
- Pressure regulation and Supply system.

6.1.2 PSA Based Oxygen Generation Plant or Oxygen Concentrator

When Ozone is produced with Oxygen, the concentration of Ozone is higher (6- 12% wt %) and Ozone so produced is pure. Ozone produced with oxygen is preferred in several applications including packaged water treatment system. Present set up is with a P.S.A. based Oxygen Generating Unit. Latest generation high-performance Ozone generators run on Oxygen feed gas.

As the Oxygen Plant is made in MS Epoxy Coated material. Preferable in an area where humidity levels are not more than 40%. Air compressor for the Oxygen Plant is to be kept close to the Oxygen PSA System, further if the area is enclosed it is recommended to provide a Exhaust duct for the Compressor so that environmental temperature of the enclosed is not increased due to the heat dissipated by the compressor exhaust. As the Oxygen Plant needs fresh air for generation of Oxygen, proper ventilation must be provided in the area where Oxygen Plant is installed.

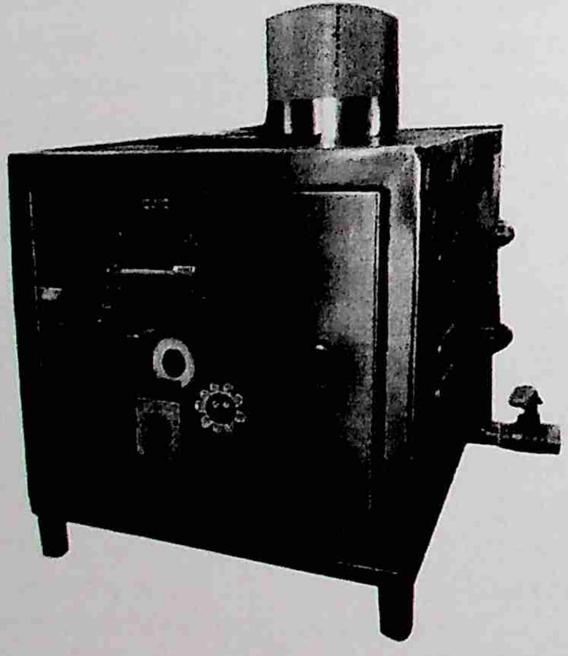


- PSA Oxygen Generation Unit

Oxygen concentrator is an on-site Oxygen production equipment where the separation of Oxygen from air is accomplished by PSA (Pressure Swing Absorption) principal. Beaded inert ceramic material (Molecular Sieve) is used for absorption of nitrogen from air. In actual operation there are two cycles, Absorption and Regeneration. During regeneration cycle, absorbed nitrogen is rejected to environment and subsequently in absorption selectively Nitrogen & moisture is absorbed. The outgoing gas has high percentage of oxygen (90-97%). The Molecular sieve used for selective separation has a long working span and does not require replacement for several years e.g. 7 to 10 provided necessary precautions are observed during operation of the plant. The process is completely regenerative making it reliable and virtually maintenance free.

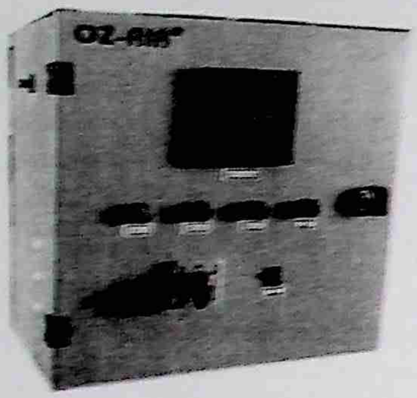
6.1.3 Closed Loop Water Chiller

Closed loop water chiller is to be located close to the Ozone Generator, further source of water must be connected to the system, as it automatically takes water as & when required. NOTE: The quality of water to be used in the water chiller must be soft or low TDS water, so that the Water loop of Ozone di-electrics will not be clogged or chocked.



6.1.4 Ambient Air Ozone Monitor Controller

As this monitor is used for Monitoring Ozone Concentration in environmental air, in the Area where Ozone Gas is used, thus it is recommended to install Ozone Ambient monitor & controller in all the areas where Ozone generation is done or is used in the process. Set points of Relay is set as per requirement depending upon working of personals in subsequent areas.



6.1.5 Dissolved Ozone Monitor Controller

Ozone Dissolved Monitor & Controller is used for Measuring Ozone Dissolved in water, this monitor is to be used for online measurement, thus Ozone dissolved monitor & controller is to be mounted on the sampling line with Manual & Electronic Solenoid Valve in the water line where Ozone is mixed & concentration of Ozone is to be controlled or monitored.

6.1.6 Vent Ozone Destructor

When Ozone is mixed in Ozone reaction Tank, Ozone is mixed partially in water and some leftover Ozone is vented out of tank, for safe guarding Ozone concentration to go above the limit it is recommended that Ozone vent Destructor is mounted at the vent of Ozone Reaction tank, which decomposes Ozone to oxygen, making exhaust air free form Ozone.

TRACEABILITY OF THE TEST INSTRUMENT

The Instrument used for Calibration is Digital Ozone Meter, Model No. BMT-965 ST, Serial No. #150000416 tested and approved by M/s BMT Messtechnik GmBh, Germany. Vide their Test Report dated 02.07.21 valid up to 01.07.22.

<u>TEST CONDITIONS</u>

- Equipment : Ozone Generator
- Model : OZ-AIR® ILG 150 OXY
- Rated Output : 150 gm/hr

Test Conducted at Following Parameters

- Gas Flow : 25 LPM ~ 1.5 m^3/hr
- Feed gas Oxygen Concentrator : 93%
- Dew Point at feed gas : -60^{O}C
- Gas Supply Pressure : 0.5Kg /cm^2
- Cooling water flow : 300 lit/hr
- Supply specifications
  - System Voltage : 220-230 Volts
  - Max. Gen. Current : 7 – 8 Amp

Ozone Generator Parameters (At 3.5 m^3/hr Flow)		Ozone Output	
I/P Signal Volts	Power (KW)	gm/m^3 (Conc.)	gm/hr (Output)
1	165	25.1	15.0
2	330	50.1	30.1
3	495	75.2	45.1
4	660	100.3	60.2
5	825	125.3	75.2
6	990	150.4	90.2
7	1155	175.5	105.3
8	1320	200.5	120.3
9	1485	225.6	135.4
10	1650	250.7	150.4

INLET OUTLET FITMENTS

- Ozone Line : 12 mm silicon
- Feed Gas Line Diameter : PU 8
- Water Line inlet/outlet : 12 mm PVC Braided

PILOT SCALE OZONE REACTOR

This customized, Pilot Scale Ozone Reactor – Continuous System is used for Treating the Pulps, Using Ozone Gas (O_3) in such a manner, that the Transfer of Ozone Gas will be achieved efficiently from Gas to Solid & Liquid.

The Reactor has provided, complete with the following Features –

6.2 MAIN FEATURES:

- Main Unit on Sturdy Staging Base,
- Horizontally Fitted Cylindrical Vessel,
- Screw Feeding System, Material Release Valve,
- Specialized Scrolls,
- VFD & Motor mounted,
- Electrical Heaters & Vessel Insulation,
- Ozone Injector Pump,
- Distribution Chamber & Perforated Screen,
- Safety & Pressure Release Valves,
- Temperature Sensor & Pressure Gauge.
- Control Panel complete with Start, ON & OFF Switches.
- PID Temperature Indicator Cum Controller.
- Platform with Steps.

6.3 TECHNICAL SPECIFICATIONS Model No. UEC-CSTMIZ/PSOR/021

DETAILS OF UNIT
The Vessel - 01 No.
Length – 1200 mm Approx.
Diameter – 150 mm Approx.
Wall Thickness – 7 mm Approx.
Volume – 21 Ltr. Approx.
Pulp Capacity – 0.75 Kg/ Hr. to 1.5 Kg/ Hr. Approx.
Pulp Consistency – 8% to 30 % Approx.
MOC with Test Certificate. - S.S. 316L. Along with Contact Parts.
Insulation – Through Heat Proof Muffled Jackets.
Heating - Electrically, Through Jacketed Heaters.
Temperature Control – Electrically (+/- 1° C)

Feeding System: -
Feeding – Through Specialized Feeding System.
Variable Speed - Selectable through VFD
Ozone Leakage Safety – Through Pneumatically Close Valve.

Scroller –
Specialized Scroller - (MOC - S.S 316L) Fitted inside the Vessel
(Auto Reversible Scroller with Time Set.)
Variable Speed - Selectable through VFD
Ozone Leakage Safety – Through Specialized Seals.

Temperature
Display– Digitally, Through PID.
Temperature Range – Ambient to 200°C. with **Sensor**

Pressure
Readout Gauge -Tested, Bourdon Type Pressure Gauge, Mounted on the Vessel.
Pressure Range – Atmosphere to 15 Kg/cm².
Release & Safety – Through Adjustable Pressure Release & Safety Valve.

Ozone Gas Inlet
Inlet – Through Specialized Ozone Injector Pump.
Distributor Chamber with Perforation.
Pneumatic Sealing Valve at Feeding, Release Valve, Specialize Seals

Cooked Material Outlet
Motorized / Specialized Valve

Control Panel:
1= Speed set & Display for every drive
2= Timer
3= Ozone mixing Switch
(Valve will be operate pneumatically through actuator)
4= Line ON/OFF
5= Start and stop switch
6= Emergency Stop Button
7= Temperature control & Display

Conclusion

Under the project "Demonstration of Ozone treatment technology of indigenous raw material pulp at pilot plant scale core objective of the project id to develop pilot scale ozone reactor for treatment of pulp in horizontal reactor, simulating the commercial reactor for large sample size of pulp at various consistencies.
The objective was fulfilled and ozone reactor, ozone generator and oxygen plant were procured and integrated at PCPB division. The trial of ozone treatment for pulp were carried out successfully.

Future plan

In future a project on fabrication of reactor for mill scale demonstration of larger capacity can be installed.
A proposal in this line will be prepared and submitted to RSC or other agencies.

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Response of Ozone Bleaching on wheat straw and bagasse mixed Agroresidue Pulp





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Abstract

Enviornmental regulations and the competitiveness of pulp production are very often in conflit with each other. Due to this capability to partly or totally replace chorine-based chemicals, ozone bleaching offers a unique opportunity to meet both these goals. Reduction of fresh water usage and limitation in effluent laod are already "external' driving forces for long-term sustainability in pulp production. Ozone has proved to be one of the best green oxidant to reduce environmental loads in terms of AOX, COD emission and quality of fresh water usasge. Ozone bleaching is not a new tehcnology but is a well proven technique. The green bleaching solution developed has been shown to offer extensive bleaching chemical saving whilst meeting pulp quality standars.

Ozone bleaching technology is in nascent stage of Indian Paper Industry. One wood basedpaper mill in southern India has installed ozone stage in bleaching line. The present study covers the response of ozone bleaching on mixed agro residue pulp collected from M/s. Naini Paper Mills Ltd., with a furnish of 50% bagasse and 50% wheat straw pulp. The study incorporated the effect of variables viz consistency, mixisng speed i.e. rpm, time and temperature on efficacy of ozone in terms of brightness nad viscosity of pulp. The effect of ozone bleachaing on effluent characteristics and their load has also been studied in comparision of conventional system used in agro bassed mills.

Till date application of ozone bleaching technology has not been implemented in any of the agro resude based pulp & paper industry in India. The reason behind this is the fact that ozone is considered as less selective as compared to chlorine dioxide. The present study is helpful in understanding the effect of ozone bleaching on agro residue raw matrerials pulp under different operatiang conditions and response of different sequences of ozone bleaching of the agro residue based pulp w.r.t. pulp quality.

Introduction

The strong consideration for environment safty as well as production of a pulp and paper following green process is to days demand. The production of bleached pulp which [illegible] considered as most polluting business as compared to other [illegible] are compelled to adopt environment benign technologies. [illegible] chemistry is the concept based on utilization of such [illegible] which does not left any toxic byproducts after completion [illegible] bleaching process of pulp conventionally utilizes [illegible] chlorine dioxide, hypo has substitute in the form [illegible] and hydrozen peroxide. These chemicals are [illegible] oxidants and are equally efficient as of their [illegible] ment like chlorine dioxide and hypo and does not left with any toxic byproducts in the environment and make production cleaner.while oxygen and hydrogen peroxide are proven technology, ozone bleaching technology is in development stage.

Fundamental Aspects of Ozone Bleaching:

Ozone has an electrophilic character that promotes reaction with functional groups in the lignin. Aliphatic double bonds conjugated to the aromatic rings in stilbene, styrene, and enol ether structures will form epoxides or ozonides, or further form

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carbonyl groups and hydrogen peroxide when reacts with ozone. The ozone reaction can also happen by insertion of an oxygen atom into carbon-hydrogen bonds in alcohol aldehyde- and ether- type structures therefore disintegrate the lignin structure. In general the ozone reacts with structures in the lignin to form functional groups therefore change the macro molecular structure of the lignin. It was found that ozone appears to be more efficient than chlorine dioxide and hydrogen peroxide in inducing the formation of carboxylic acid from residual kraft lignin [1].

Ozone itself found to be 106 times more reactive to lignin than to carbohydrates. However, the by-products from those reactions of are easier to react with carbohydrates. The nature of this reaction leads to a hypothesis that pulp with high lignin will sustain more on viscosity loss than low lignin pulp.

The critical parameters to determine the amount of ozone added to remove lignin are lignin removal (measured by kappa number or optical properties) and carbohydrate degradation (measured by pulp strength or by viscosity). These two parameters will be used to express the effectiveness of ozone delignification and its selectivity.

The main process variables that influence the effectiveness and selectivity of ozone delignification are pulp consistency, ozone charge, pH, time, temperature, chemical additives, effects of metal ions, residual organic matters and pulp treatment before an ozone stage. A rapid and efficient transfer of ozone into appropriate fibre constituents is very important to enhance ozone-lignin reaction instead of cellulose decomposition [2].

Much of early ozone bleaching works on low (0.5–3%) and high (30-40%) stock consistency. Low consistency allows optimum mixing. In the high consistency maximum exposure of fibre surface to ozone is achieved by fluffing to separate fiber aggregates to the greatest extent possible. The most efficient delignification for ozone bleaching occurs near pH 2. In high consistency ozone bleaching, acid treatment prior to bleaching can remove metal ions from pulp, while acids brings H+ that replace M+ in the pulp (2). Alkali extraction stage after ozone bleaching is purposed to reduce kappa number of ozone-delignified pulp. Alkali has an important role to remove lignin from pulp.

Ozone bleaching gives additional possibilities to reduce the kappa number of pulp before final bleaching. The powerful delignification and brightening capability of a high consistency ozone stage allow for a significant reduction in total chlorine dioxide use for an ECF bleach plant.(3).

Worldwide scenario of Ozone Bleaching technology:

The industrial use of ozone has already undergone a long string of improvements and developments. Like other new technologies, ozone bleaching did not immediately reach its optimal technical efficiency but faced several issues during its early years. Achievements of ozone bleaching have improved year in year out and it is now a well proven technology for bleaching of unbleached pulp.

Ozone (O_3) was introduced in the bleaching of chemical pulps in early 1990s. Since then, about 30 bleach lines containing ozone have been installed. The first industrial pulp bleaching line including an ozone stage started ~25 years ago. Among those 22 mills [illegible] produce solely hardwood pulps, 4 produce both softwood and hardwood pulps while SCA in Östrand (Sweden) and Rosenthal in Blankenstein (Germany) produce exclusively softwood pulp.

Ozone bleaching is efficiently used on hardwood and softwood pulps, on kraft and sulphite pulps dedicated to all kinds of final applications. Pulp producers do not always evaluate the significant ecological advantages of ozone-based bleaching sequences over the traditional ECF bleaching sequence D0-Eop-D1-D2 (or its variants). Sweden, Brazil, Japan, Finland and USA are among the countries where ozone stage in bleaching sequence.

This proves that Z-ECF bleaching fulfils all the requirements to be the best available technology (BAT) for "green" bleaching: it is a well-proven tech-nology with significantly lower operating costs.

Eucalyptus pulp is being bleached as single species or as a mixed hardwood pulp, with ozone in more than 10 mills around the world including Brazil bleached as a single Eucalypts, Japan, Australia, India and Europe. Most of these mill use ECF sequence with ozone as such as

1. ZeDP where Z is a high consistency ozone bleaching stage followed by dilution to medium consistency and allow for an extraction stage e stage to take place without intermediate washing.
2. Z/DEOP-D where Z/Das a medium consistency ozone bleaching stage Z followed directly by a chlorine dioxide stage D with intermediate washing.

Modern bleaching technologies and Indian Paper Industry:

In terms of modern technology adoption the Indian wood based mills are continually replacing the conventional pulping and bleaching technologies with newer fiber line. After installations of Oxygen delignification and ECF technology, Indian paper industry is now setting goal for further developments available there. Installation of Ozone stage in ECF line in one of the state of art integrated pulp and paper mill in south India i.e. ITC Ltd. Bhadrachalam is example of this.

Indian paper industry is always eager to adopt the new technological developments which took place in the past to make the bleaching process more envoronment friendly and economical viable. Unlike other developed countries India has variety in raw materials with a very wide range. On one hand there are hardwoods viz eucalyptus, subabul, acacia etc. on other hand agroresidual raw materials mainly bagasse and wheat straw contribute substantial quantity in fiber deficit country.

The response of any new technology on different raw materials always varies. Though the laboratory scal reponse of new bleach chemical is very good but technologically it not replicate in same manner one example of this is oxygen pretreatment technology, which has successfully adopted by hardwoods, but nor has very good response on agroresidual fiber, though in laboratory scale trials the response is always very good.

The ozone bleaching technology could not be adopted as was oxygen pretreatment technology there are number of merits which support the ozone bleaching technology. Only one pulp and paper mill ITC PSPD has install ozone bleaching in their fiber line.

Ozone bleaching technology for agroresidual raw material will not only support in the reduction of effluent load but more feasable in terms of ease of adoptability of this technology.very limited study are reported on ozone bleachin of pulp for agroresidual raw materials so far.(2,5)

In the present paper the efficacy of ozone bleaching in view of various process parameters like mixing speed and consistency of pulp has been studied.the study has been conducted on pulp collected from Naini Tissues Ltd.The unbleached pulp has composition of bagasse and wheat straw in ratio of 50:50.

Experiemtal

Experiments on ozone bleaching were carried out in quantum mixture IV of quantum technology Inc Ohio.Quantum mixture has facility of mixing the pulp at different RPM.the two vary important parameters viz. effect of consistency and mixing speed has been studied.

The quatum reactor has vassel of 3500 ml capacity with shaft in the bottom for mixing. A sample size of 100-350 gram of pulp can be taken at 3-25% consistency. The mixing rpm may be selected from 1-2500 rpm. The selection of sample size depends on the consistency and mixing. For proper mixing efficiency at medium consistency a sample of minimum 150 gm is selected.

Results and Discussion

Characterization of Mill Pulp

The results of ODL pulp charachterization are depicted in table 1.

Table 1: Charachterization of Mill Pulp (after Oxygen pretreatment stage)

Parameters	Unit	Results
Kappa number	---	9.6
Pulp brightness	ISO (%)	54.5
Pulp viscosity	cc/g	808
Freeness	ml CSF	480
Tear Index	mN.m²/g	6.2
Tensile Index	Nm/g	39.2

The mixed agroresidue pulp collected from Naini tissues Ltd has good brightness after ODL i.e. 54.5 and initial viscosity 808 cm³/g at kappa number 9.6. The tear and tensile index are also fairly good after ODL treatment.all results are depicted in table 1.

Effect of mixing speed on characteristics of the pulp

The ozone is a fast reacting ozone require proper mixing hence an optimum mixing has to be maintained for effective reaction of ozone with lignin in cellulosic fibre bundle. Initially a blank pulp without ozone was given different mixing speed like 120, 240 and 600 rpm the effect of various mixing speed on pulp properties has given in table 2.

Table 2: Effect of mixing speed on characteristics of the pulp.

Parameters	Control pulp	1	2	3
Consistency		5%		
Mixing speed RPM	-	120	240	600
Pulp Brightness (% ISO)	54.5	53.7	54.0	53.9
Kappa No.	9.6	9.3	9.1	8.8
Pulp viscosity cc/gm	808	760	749	738
Pulp freeness, ml CSF	480	458	450	445
Tear index (mN.m²/g)	6.2	5.7	5.5	5.2
Tensile index (Nm/g)	39.2	42.1	42.7	43.1

Considering the effect of mixing at various rpm it has been observed that 240 rpm is sufficient as there is marginal impact of this mixing speed on pulp properties as compared to control.

Comparison of different TCF bleaching sequences at 5, 12 and 35% consistency

It is very important to have proper mixing of pulp. The effect of ozone reaction with lignin is reflects in terms of brightness gain. Like chlorine treatment ozone also instatly bleach pulp which can be seen in gain of brightness after final bleaching of pulp (table 3).

The reaction of fast reacting ozone with agroresidual raw material pulp has effect of consistency. As shown in table 3 a detailed study of various TCF bleaching sequences on final pulp properties viz brightness is increased with consistency from 5 to 35%. At higher consistency brightness found to be better. A very intresting fact is that the short sequence TCF bleaching of agroresidual pulp with AZ(EOP), AZP, AZ(EP), ZP and AZ(Ep) sequence is also effective to reach pulp brightness at optimum level of around 86%ISO brightness.

The TCF sequences have additional benefit in terms of NPE free effient which may de diverted to washing of unbleached pulp and support the bleach plant to achieve the Zero Liquid Discharge. The stength propertes are negatively affects with increased consistency and hence it is better to opt medium consistency 12%.

Characteristics of Effluent generated during lab scale Ozone bleaching of pulp

Table 3: Comparison of different TCF bleaching sequences at 5, 12 and 35% consistency.

Parameters	AZ (EOP)			AZP			AZ (EP)			ZP			AZ (Ep)		
[illegible]	5	12	35	5	12	35	5	12	35	5	12	35	5	12	35
Final pulp brightness, % ISO	84.5	84.2	87.6	82.6	83.0	86.6	81.3	81.7	86.8	81	80.7	83.0	78.4	79.1	86.1
[illegible]	580	575	501	610	562	523	595	546	528	610	585	530	612	598	544
[illegible]	0.12	0.13	0.33	0.50	0.48	0.21	0.15	0.13	0.26	0.5	0.53	86.0	0.2	0.18	0.20
[illegible]	6.16	6.09	5.6	6.1	6.23	5.4	6.17	6.34	5.4	7.0	6.25	5.2	6.5	5.78	5.1
[illegible]	28.6	37.5	35.0	31.0	37.5	36.2	30.8	39	37.4	32.9	44.3	36.5	32.1	38.3	36.8

The effect of ozone in bleaching of pulp has also been observed and has shown in table 4.

Table 4:Characteristics of Effluent generated.				
Bleaching Sequences	COD, mg/l	Total suspended solid, mg/l	TDS, mg/l	Color, ptc, number
AZP	603	190	3306	3
AZ (Ep)	745	174	2678	7
AZ (EP)	1133	216	2660	16
AZ (EOP)	1192	228	2740	23
OZP	562	180	2850	13
CEopH	1343	193	3495	34

Conclusions

- Detailed study of process parameters like mixing RPM and consistency was carried out on pulp collected from Agro based mills.The mixing speed at 250 RPM is optimum and was taken for experiments.
- The effect of consistency indicates that medium consistency 5 and 12% have not much variation in brightness gain during various TCF bleaching sequence.
- Ozone based TCF bleaching of wheat straw bagasse mixed pulp was carried out following 5 different sequences. Among the AZP, AZEp, OZP, AZEP and AZEOP the last TCF bleaching sequence AZEOP has shown best brightness target than other sequences.
- It is possible to achieve +85% ISO brightness after introduction of Ozone in bleaching sequence.
- Effect of medium (12%) and high (35%) consistency is quite distinguished in term of pulp final brightness gain which is higher in case of high consistency.
- It has been concluded that short sequence TCF bleaching of Agro-residues with combination of Z and P is also possible and can be adopted at commercial scale.
- As expected the PC Number of ozone based TCF sequence is ~90% less than conventional CEopH bleaching.
- The effluent load is low and so the reduction in cost of effluent treatment is possible after introduction of ozone in bleaching sequence.
- The post ozone washings can be diverted to post BSW conveniently because of absence of NPE which opens a path to achieve targets of bleach plant closure.
- The technology demonstration with the International experts under the UNIDO project and encouraged findings in respect of quality of the pulp as well as reduced pollution load in the bleach effluents in respect of color adopting e ozone bleaching in agro based pulp should help in improving the overall sustainability of the Indian paper industry.

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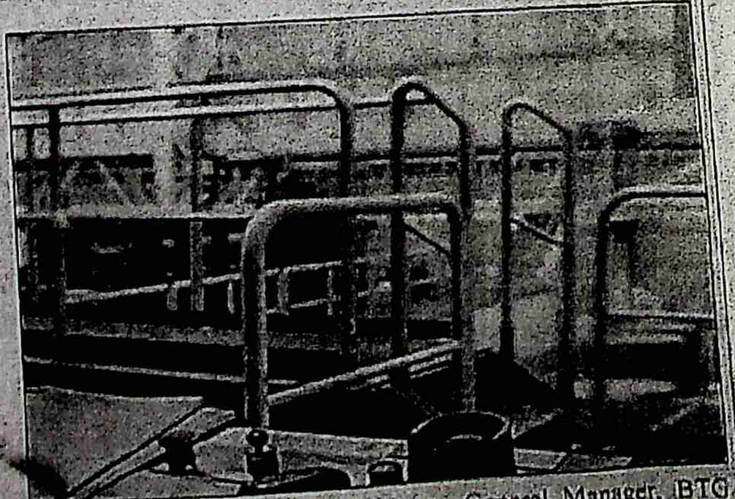
BTG to supply all specialty process measurements for JK Paper pulp mill and new board machine project

JK Paper, one of the largest pulp & paper producer in India has [illegible] BTG to supply all the specialty process measurements [illegible] the planned relocation of pulp mill and the new board [illegible] project at their Central Pulp mill, Songadh, Gujarat site. [illegible] innovative technologies combined with their strong [illegible] been known to us for decades. We are excited [illegible] fiber line measurements from BTG to help [illegible] quality for our paper and board machines at [illegible] We look forward to co-operating with BTG for [illegible] of our project" says Mr N.K Agarwal and S K [illegible]

[illegible] to be entrusted with this strategic project [illegible] committed to delivering industry [illegible] application expertise and proactive [illegible] We look forward to supporting a flawless [illegible] our long-term relationship [illegible] with JK Paper" shares Keith Waters, General Manager, BTG Group, ASPAC.■



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Environmental impact of Application of Ozone bleaching for production of pulp from agro based fibrous materials - An innovative approach

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Abstract - The pulp and paper sector is facing various issues due to environmental regulatory pressure and expanding market demand, and it is searching for novel solutions to improve product quality and process performance while reducing environmental effects during pulp bleaching. Oxygen delignified wheat straw pulp of kappa number 9.5 was subjected to conventional $CEopH_1H_2$, elemental chlorine free (ECF) i.e. $D_0E_pD_1$ and ozone bleaching sequences at different consistencies to get a final pulp ISO brightness of 85 ± 2% and evaluation of the physical strength properties of the pulp. The effect of green bleaching was also compared with the conventional and ECF bleaching of wheat straw pulp for their pulp characteristics and physical strength properties. The effect of ozone bleaching of wheat straw pulp on bleach effluent characteristics and their load has also been studied and compared with conventional ECF bleaching system used in agro based mills. The present lab study is helpful in understanding the effect of ozone bleaching on agro based raw material pulp in terms of pulp quality. Less consumption of bleaching chemicals with no effluent load demonstrates that ozone is indeed the bleaching chemical of the future for sustainable growth of the Indian pulp and paper industry.

Key words: Wheat straw pulp, Conventional, ECF, Ozone bleaching, Physical strength properties, and Effluent characteristics.

sheets were prepared using a sheet former. The bleached pulp sheets were pressed, and air dried in atmospheric conditions at 27±1 °C and a relative humidity of 65±2 %. The mechanical strength properties were measured using the standard test method i.e. bulk (ISO 534:1988E), burst index (ISO 2758), tensile index (ISO 1924), tear Index (ISO 1974 and P.C. number – CPPRI test method. The Post color (P.C.) number is defined as the brightness reversion of bleached pulp [18] and is calculated by brightness before and after aging. The aging of bleached pulp was determined by putting the pulp sheet in an oven at 105 °C for 4 hours as per TAPPI UM200. The post colour number of bleached pulp was calculated as per equation 1:

$$\text{P.C. number} = \left(\frac{(1-R2)^2}{2R2} - \frac{(1-R1)^2}{2R1}\right) * 100$$

Where R_1 is the brightness before the aging test and R_2 is the brightness afterward

Methods and bleaching conditions

Conventional and ECF bleaching sequences were applied to wheat straw pulp in the laboratory, i.e.$CEopH_1H_2$ and D_0EpD_1 respectively. Bleaching conditions are as follows.

Chlorination (C) stage:

The bleaching experiments were carried out in the laboratory-using batch vessels immersed in a constant temperature bath. The bleaching sequences employed by $CEopH_1H_2$ and $D_0E_pD_1$ were used for oxygen delignification of wheat straw mill pulp. The bleach filtrates were collected for tests. The steps are as follows: Chlorination bleach liquor was used to generate chlorine gas inside the container in which pulp was added. The gas was produced as a result of a decrease in pH<2 which was kept at around 1.5. After retention time, this pulp was washed and subjected to a alkali extraction stage reinforcement with a hydrogen peroxide stage. All the conditions, except the chlorine dose for the above-mentioned experiments, were kept constant.

Extraction followed by Hydrogen peroxide stage:

Chlorinated lignin derivatives are to be extracted out of the pulp by addition of alkali and hydrogen peroxide chemicals. The alkali and hydrogen peroxide chemical charges were applied at 2.5% and 1% respectively with 2 kg of oxygen pressure. After giving a certain amount of retention time, the pulp was washed.

Hypo chlorite H_1 and H_2 Stages:

The extracted wheat straw pulp is mixed with hypo liquor (40-50gpl) and the pH was maintained above 9-10. All the process conditions were maintained as in the figure 1.

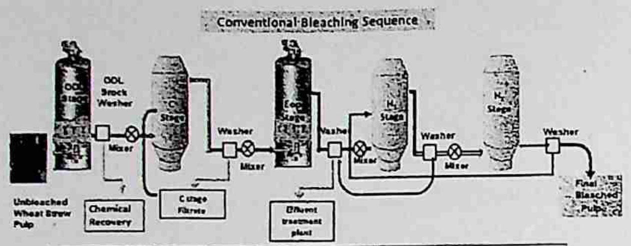
1. Introduction:

Bleaching of agro pulp has become an environmental issue due to more stringent laws against pollution generated by Indian pulp and paper industries and the release of adsorbable organic halides (AOX). Chlorine based pulp bleaching generates chlorinated organic compounds which accelerate degradation of acute or even chronic toxins and can induce genetic changes in exposed organisms [1],[2]. The recent trend in bleaching is to shift to elemental chlorine free (ECF) bleaching, i.e. replacing elemental chorine with chlorine dioxide. Chlorine dioxide is a strong oxidant. It has 19 valence electrons, thus, consisting of free radicals. The sensitivity of free radicals present in chlorine dioxide bleaching chemical probably also accounts for its high reactivity as an oxidizing agent used for pulp bleaching. It is specific in reacting with lignin structures of pulp by which lignin gets oxidized. ECF bleaching is more selective which preserves the strength of pulp and at the same time provides high brightness stability with lower effluent load in comparison to the conventional $CEpH_1H_2$ bleaching sequence. The promotion of ECF and total chlorine-free (TCF) bleaching techniques has focused on reducing AOX and total organic chlorides (TOCl) in bleach effluents [3], [4], [5], [6]. TCF bleaching techniques considerably decrease the bleach effluent load which provides the scope to make a closed cycle loop system of water. Actually, TCF bleaching process is the culmination of various technologies i.e oxygen, ozone, hydrogen peroxide, and different other peroxygens. Ozone (O_3) is a very high oxidizing potential agent for bleaching of pulp [7]. Worldwide, since 1990s, it has been used as a bleaching chemical on a commercial scale. Globally, around 25 paper mills were using ozone gas as a bleaching chemical to bleach their pulp [8]. Ozone is very effective delignifying agent for bleaching wood and non-wood chemical pulps. It can be used by ECF and TCF bleaching sequences at different consistency levels [9], [10], [11], [12], [13], [14]. To produce 1 kg ozone gas, 8.3 kg oxygen and 10 kwh power is required. In addition, ozone is a highly viable bleaching chemical which is one and half times less expensive than chlorine dioxide. Only 5–6 kg of ozone is required to bleach 1 ton pulp because ozone is 106 times more reactive to lignin than to carbohydrates [15]. During ozone bleaching intermediate radical formations takes place which vigrously attack on carbohydrates that reduces the pulp viscosity [16], [17]. Ozone is an emerging green bleaching practice and favoring on-site chemicals production. TCF based ozone bleaching process is an option to reducing the effluent load as the filtrate from the ozone stage and further extraction stage can be circulated back to the recovery boiler. Ozone is an efficient bleaching agent for the bleaching of wood and non-wood pulps. Ozone can delignify both the wood and non wood chemical pulp when used at low, medium- and high-pulp consistencies in ECF and TCF bleaching. The present study investigated the effects of ozone bleaching on agro wheat straw pulp using conventional ($CEopH_1H_2$), and ECF (D_0EpD_1) bleaching sequences, under optimum process parameters. It was also compared with the TCF bleaching sequence i.e., AZEOP (pressurized) under variable process conditions i.e. pH, fixed ozone dose, ambient temperature, lower to higher consistencies i.e., 5%, 12%, and 35% and fixed rpm 240 to get a final pulp ISO brightness of 85± 2%. The bleached pulp properties, physical strength properties and effluent characteristics were evaluated for all bleaching sequences. For a closure loop system and to mitigate bleach plant effluent load, it is essential to adopt the ECF and TCF bleaching technologies. The implementation of ozone based technologies considerably reduces the generation of hazardous effluent and provides a greener processe for bleaching. It will also help the pulp makers to meet the environmental regulation water norms on the discharge of bleach effluent.

2. Experimental:

2.1 Material and methods

Agro based wheat straw pulp after oxygen delignification stage was received from the pulp and paper mill and stored in the refrigerator at 4°C for carrying out conventional $CEopH_1H_2$, elemental chlorine free D_0EpD_1 and ozone bleaching AZ(EOP) experiments in the lab to get a target ISO brightness 85±2%. The following standard methods were used to characterize wheat straw pulp, and bleached pulps for various parameters: Kappa number TAPPI T 236-OS-76; Pulp viscosity SCAN C 15: 65 and Pulp brightness ISO 2470-1- 2016(E). 60 g/m^2 bleached pulp hand

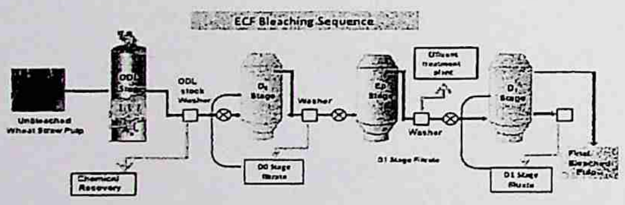


Bleaching Stage	C	Eop	H_1	H_2
Time - min	45	60	120	120
Temperature- °C	Ambient	90	80	80
Chemical -kg/O.D. metric ton bleached pulp	23	20	7	2
pH	<2.0	11-12	9-10	9-10
Pulp consistency	3	8	8	8
Pulp brightness %(ISO)	57.2	77.1	81.4	85.1

Fig.1. Graphical representation of conventional bleaching sequence i.e., $CEopH_1H_2$

Chlorine dioxide stage:

Chlorine dioxide bleaching chemical, 40-50 gpl strength, was prepared in the lab using sodium chlorite, acetic acid, and sodium acetate. This solution was added to pulp. The pulp inlet pH of 2-3 was maintained in the D_0 stage, whereas 3-4 in the case of D_1 stage. Chlorine dioxide D_0 and D_1 stages were performed in the polyethylene bags using a water bath. The bleaching chemical of chlorine dioxide was used as D in D_0 and D_1 bleaching stages at 2% and 1%, respectively.



Bleaching Stage	D_0	Ep	D_1
Time - min	45	60	180
Temperature- °C	70	70	80
pH	2.0-2.5	11.5	2.5-3.0
Chemical -kg/O.D. metric ton bleached pulp	20	15	10
Pulp Consistency	5	8	10
Pulp Brightness %(ISO)	59.4	78	86.2

Fig. 2. Graphical representation of ECF bleaching sequence i.e., D_0EpD_1

Total chlorine free bleaching:

The oxygen delignified wheat straw pulp was bleached using AZ(EOP) under optimized bleaching conditions. The AZ(EOP) bleaching sequence was carried out at three different pulp consistencies of 5, 12, and 35% as follows.

Acid stage (A):

Prior to ozone treatment, the pulp was thoroughly mixed with water and sulfuric acid then preheated to the desired temperature in a microwave oven and placed into a temperature-controlled heating bath to maintain a pulp consistency of 5 % for 45 min. After the completion of the desired reaction time, about 300 mL of liquor was squeezed out from the pulp for pH analyses. The acid treated pulp was taken for further bleaching experiments.

Ozone strength determination:

The strength of ozone was determined using the following steps; Take 200 ml of KI solution and 100 ml 4N H_2SO_4 solution are added in impinger glass bottle with bubbling the sampled air at low flow rate ; a second impinger glass bottle is joined in series as a guard detector for ozone transfer and reaction in the bottle; ozone generator at a flow rate 5LPM gas pass in acidified KI solution for 1 min immediately titrating against standard solution of freshly prepared 0.1 N $Na_2S_2O_3$ using starch 0.5ml of the starch indicator until solution pale yellow color become colorless.

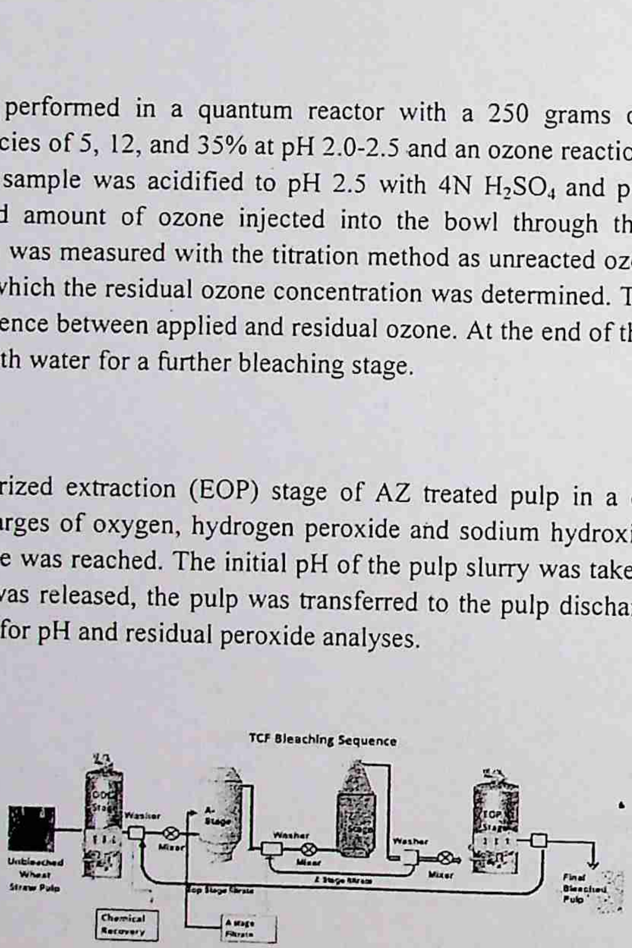
Ozone concentration in gpl = 24 x volume of $Na_2S_2O_3$ in ml x 0.1Normality of $Na_2S_2O_3$ divided by initial volume of ozone gas in liter

Ozone Stage:

Ozone experiments were performed in a quantum reactor with a 250 grams oven dried mixed pulp sample maintaining pulp consistencies of 5, 12, and 35% at pH 2.0-2.5 and an ozone reaction time of 5.0 min with a 10 min retention time. Each pulp sample was acidified to pH 2.5 with 4N H_2SO_4 and placed into the mixer bowl then supplied with the required amount of ozone injected into the bowl through the ozone generator. The ozone concentration in the stream was measured with the titration method as unreacted ozone from the pulp was collected in a 5% KI solution, after which the residual ozone concentration was determined. The ozone consumed by the pulp was calculated as the difference between applied and residual ozone. At the end of the reaction, the unwashed ozone treated pulp was washed with water for a further bleaching stage.

EOP Stage:

Figure3 depicts the pressurized extraction (EOP) stage of AZ treated pulp in a quantum reactor under various conditions. The desired charges of oxygen, hydrogen peroxide and sodium hydroxide were added into the reactor after the desired temperature was reached. The initial pH of the pulp slurry was taken. After completion of reaction time, the reactor pressure was released, the pulp was transferred to the pulp discharger and 200 mL of liquor was squeezed out from the pulp for pH and residual peroxide analyses.



Bleaching Stage	A	Z	EOP
Time - min	60	10	120
Temperature-°C	85	35-40	110
pH	2.0	2.5-3.0	11-11.5
Chemical –kg/O.D. metric ton bleached pulp	5	4.5	NaOH- 20 kg H2O2- 15 kg
Pulp Consistency	5.0	5,12,35	8
Pulp Brightness %(ISO)	46.0	68.1,69.1,72.4	81.6,82.4,85.2

Fig. 3. Graphical representation of TCF bleaching sequence i.e., (AZEOP)

3.0 Results and Discussions:

Table1 showed the initial characteristics of wheat straw pulp, viz brightness, kappa number, viscosity, and some physical strength properties. Oxygen delignification is an intermediate step applied to unbleached pulp before bleaching to reduce kappa number [19]. Maintaining a low kappa number during bleaching of pulp is beneficial for both the economics and the environment [20], [21]. In the oxygen delignification stage, the degree of delignification reaches 40-60%, i.e. kappa number reduction [22]. The physical strength properties of wheat straw pulp, i.e. the tensile and tear indices were found to be 40.5Nm/g and 6.1 mNm^2/g.

Table 1: Results of characterization of oxygen delignified wheat straw pulp

Parameters	Unit	Results
Pulp brightness	(%)ISO	47
Kappa number	-	9
Pulp viscosity	cm^3/gm	780
Freeness	ml, CSF	485
Tear index	$mN.m^2/g$	6.1
Tensile index	Nm/g	40.5

A detailed study on the bleaching sequences comparison of wheat straw pulp was carried out as shown in figure 4. The results of conventional, ECF and TCF bleaching showed that the final ISO brightness of $CEopH_1H_2$ and D_0EpD_1 bleached pulp is 86.0 and 86.5 % respectively. The pulp viscosity of D_0EpD_1 bleached is 552 cc/gm and (13.7%) more compared to $CEopH_1H_2$ bleached pulp, i.e., 476 cc/gm. Chlorine dioxide is more selective towards lignin compared to other bleaching agents; it can brighten pulp without degrading cellulose. In the $CEopH_1H_2$, chemical used is less selective than chlorine dioxide; hence the viscosity drop is more than in ECF bleaching [23].

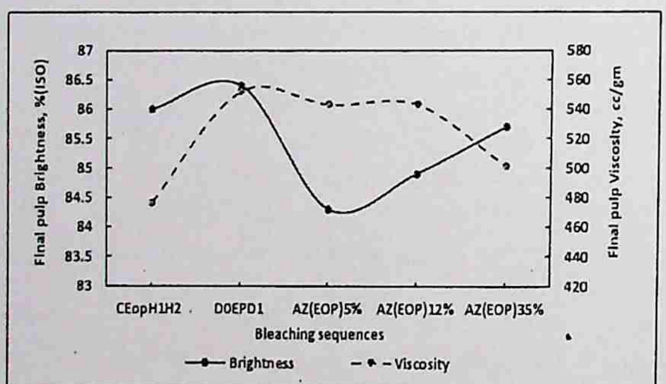


Fig. 4. Effect of different bleaching sequences on brightness and viscosity of final bleach pulp.

The post color number in $CEopH_1H_2$ is 1.53 higher compared to D_0EpD_1 bleached pulp. Post color number of D0EpD1 pulp was found to be 0.13, 0.21, and 0.32 points more than AZ(EOP) pulp, when AZ(EOP) bleaching was done at consistency of 5 %, 12 %, 35% respectively. Brightness reversion was higher in case of chlorine based bleaching due to destruction of quinine chromophores and generation modified quinones group. Similarly, high PC number was found in conventional and ECF bleaching in comparison to that found in TCF bleaching [24]. Acid pretreatment of wheat straw pulp by AZ(EOP) sequence showed minimizing soda carry over and improving performance by lowering bleaching chemical consumption was mentioned in the earlier published research work of [24]. The removal of hexenuronic acid (HexA) by acid pretreatment and the lowering of bleach chemical demand were discussed in several recent studies. Hexenuronic acids were formed when unsaturated sugars produced from hemicelluloses undergo alkaline degradation during pulping. Bleaching reagents such as chlorine, chlorine dioxide, ozone, and hydrogen peroxide were quickly consumed by these molecules. According to [25], HexA contributes around 20-60% of the total kappa number for industrial hardwood kraft pulp.

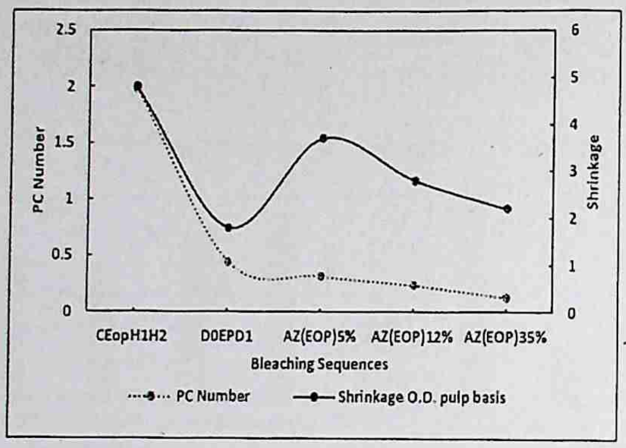


Fig. 5. Effect of different bleaching sequence on PC number and pulp shrinkage of final bleach pulp

During the ozone stage, pulp viscosity drops by 7.7 % at high consistencies of 35%, i.e. 501cc/gm. The viscosity of pulp was found to on higher side i.e. 543 cc/gm when ozone bleaching was done at lower consistency (5%). As per the earlier research work done by Lindholm, 1990a [25], it was concluded that the reaction product flows more freely in lower consistency than in high consistency bleaching. This may be one of the reasons that contribute to the lower carbohydrate degradation at low consistency bleaching than in high consistency bleaching. The final pulp brightness of the AZ(EOP) bleaching sequence was achieved at 84.3, 84.9, and 85.7% (ISO) at 5, 12, and 35% pulp consistency respectively. The value of post color number varied from 0.12 to 0.40 as shown in figure 5. During ozone treatment, ozone breaks the conjugated carbon bonds present in lignin which do not let the pulp become yellow. Ozone stage followed by EOP sequence (pressurized oxygen was used) at high temperature was the final stage of a bleaching sequence AZ(EOP). AZ(EOP) bleaching sequence showed significantly low brightness reversion compared to other bleaching sequences [26], [27]. The purpose of pressurized H_2O_2 addition in AZ(EOP) bleaching sequences was to enhance the lignin removal and brightness gain and to prevent viscosity loss. It is well known that p-quionoid in bleached pulp was mainly responsible for brightness reversion. Huls, 1999 [28] explained that chlorine dioxide creates new p-quionoid structures which enhances the chance of color reversion. Wennerström, 2002 [29] also stated that the final pressurized peroxide stage obtained maximum brightness stability. The new quionoid structures formed in the D_0 stage were destroyed in the subsequent peroxide stage at a high temperature (95°C). Conversely, the chlorine dioxide bleaching stage was not able to remove all the quionoid structures generated [26].

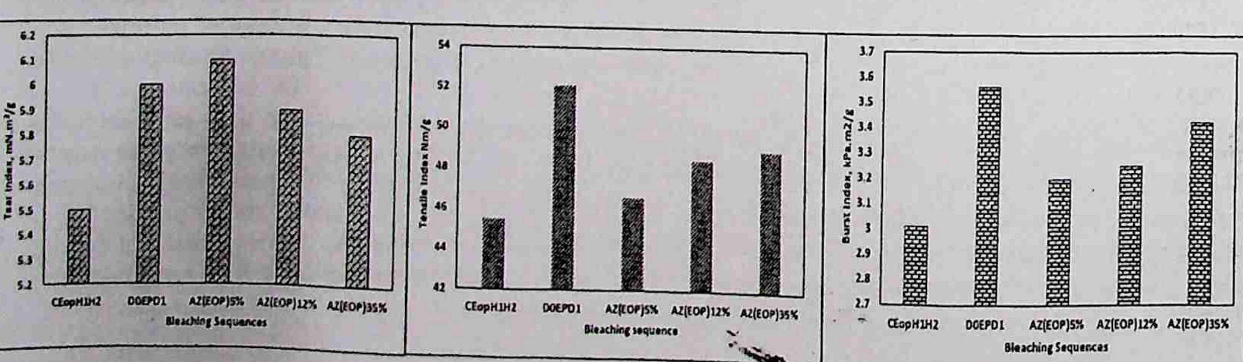


Fig. 6. Effect of physical strength properties i.e tear, tensile, and burst index, on final bleach pulp

Figure 6 showed that the $D_0E_PD_1$ bleached pulp of wheat straw showed an improvement in tear index (5.17%) and tensile index (3.55%) over $CE_{OP}H_1H_2$ bleached pulp. wheat straw pulp at 5, 12, and 35% pulp consistencies showed a tensile index of 28.6, 37.5, and 35.0 Nm/g and a tear index of 6.16, 6.09, and 5.6 mNm2/g respectively. The decrease in mechanical strength properties was due to less fiber swelling and relative bonding area. The other reason for the decrease in mechanical strength properties may be the extra degradation of low molecular weight carbohydrates after acid and ozone treatments, which adversely affects the inter-fibrillar bonding of the fiber-fiber, fiber-fines and fines-fines [30]. Zou et al. 2002 [31], demonstrated that hemicelluloses, specifically xylan, can act as protective factors against cellulose degradation and loss of strength and viscosity.

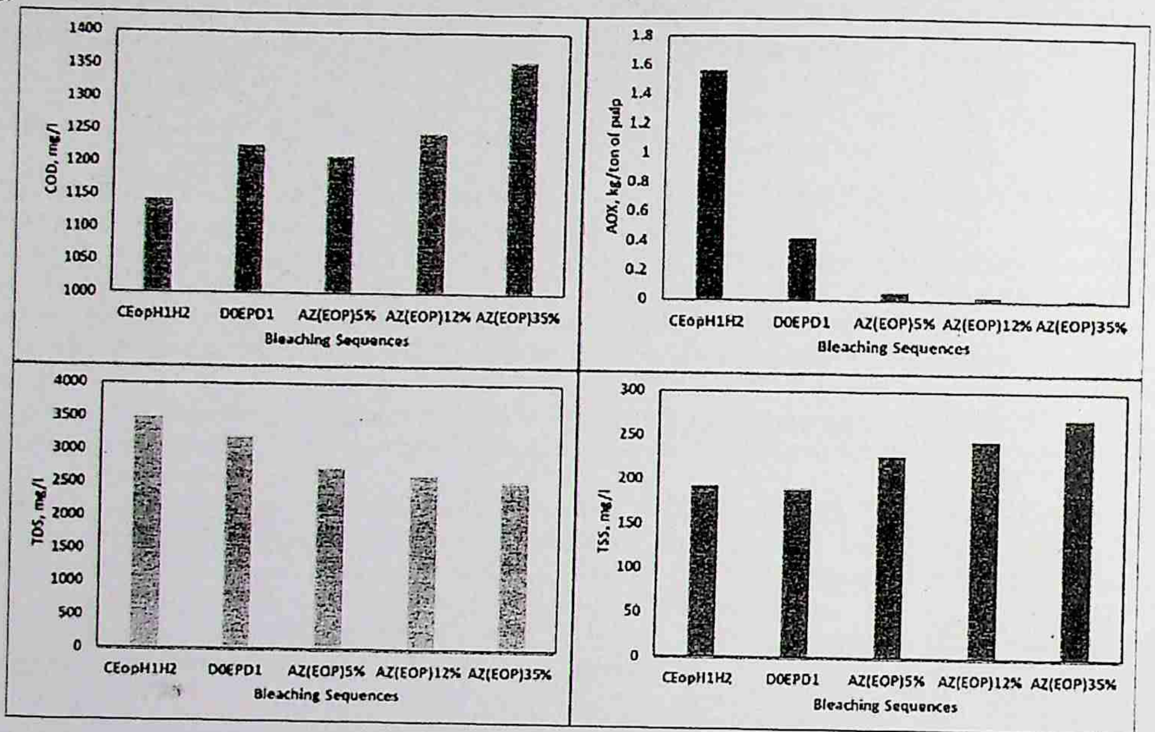


Fig. 7. Effect of bleach effluent characteristics collected in different bleaching stages i.e., TSS, TDS, COD, and AOX of different bleaching sequences.

Figure 7 reveals that the increase in COD after the AZ(EOP) bleaching sequence is more than $CEopH_1H_2$, D_0EpD_1 bleaching sequences, which indicates that removal of xylan and lignin after Z stage is more as compared to other bleaching stages. The increase in COD of bleached effluents is quite obvious in the case of total chlorine free bleaching, since, the hydrolytic action of ozone leads to the weakening of the carbohydrate bonds in the pulp and its dissolution into the media. Thus, the concentration of lignin and hydrolyzed xylan in the effluent increased markedly, which further added to the color and organic load in effluents [32], [33]. The discharge norms of COD as per the industry specific standards notified under the environmental (protection) rules, 1986 is 250 mg/l. The values achieved for COD after different bleaching sequences are higher than 250 mg/l but after the treatment of the bleaching effluent it is easily possible to achieve this range.

The AOX generation was found to be highest in case of $CEopH_1H_2$ sequence i.e around 1.5 kg/ ton of pulp. As per the industry specific standards notified under the environmental (protection) rules, 1986 the upper limit mentioned for small pulp and paper mills for AOX is 2 kg/ ton of pulp. The AOX generation was reduced to 0.4 kg/ ton of pulp by changing the bleaching sequence to D_0EpD_1 from $CEopH_1H_2$ sequence. As per the industry specific standards notified under the environmental (protection) rules, 1986 the upper limit mentioned for large scale pulp and paper mills for AOX is 1 kg/ ton of pulp. The D_0EpD_1 sequence provides lower value of AOX generation but even with

AOX in the range of 0.4 -0.5 kg/ton of pulp it is not feasible for the pulp mill to reuse the water. The above mentioned sequences directly or indirectly require the chlorine based chemicals. Therefore, there is an urgent need of bleaching sequence that is far from the chlorine usage directly or indirectly. The bleaching sequence AZ(EOP) generates AOX in the range of 0.05 to 0.02 kg/ ton of pulp at different consistency. The lower amount of AOX generated in AZ(EOP) (TCF) provides the scope of water reusage or closed loop system.

4.0 Conclusion:

- The AZ(EOP) bleaching sequence provides a way to achieve pulp brightness of 85± 1% (ISO) at variable pulp consistencies without using a chlorine based bleaching agent.
- The $CE_{OP}H_1H_2$ bleaching sequence showed ISO brightness (86 %) and lowest viscosity (490 cc/g). The maximum ISO brightness was achieved by $D_0E_PD_1$ bleaching sequence i.e 86.5. In case of AZ(EOP) bleaching as the consistency was increased from 5 to 35 %, the brightness increased by 1.4 point.
- The AOX generation in AZ(EOP) was found to be lowest at different bleaching consistency in comparison to conventional and ECF bleaching. The AOX generated by AZ(EOP) sequence was found as 0.05 kg/ton of pulp at 5 % consistency which was 97% lower than that obtained by conventional bleaching.
- The AZ(EOP) bleaching sequence can be considered as green bleaching processes because the water used in this sequence can be reused.
- The $D_0E_PD_1$ bleaching sequence improved the tear index and tensile index by 5.17% and 3.55 % than that obtained by $CE_{OP}H_1H_2$ bleaching sequence. The tensile index obtained after execution the AZ(EOP) bleaching sequence is found to be increased from 28.6 to 35 (22.6% improvement) Nm/g as the consistency was increased from 5 to 35%. Whereas in case of tear index it was vice-versa.
- Green bleaching technology is now on and a pioneering effort will continue to develop processes, especially for agro based raw materials for Indian paper mills.

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