Application Of Rice - Straw As Raw Material For Production Of Handmade Paper

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ABSTRACT

Rice Straw burning in agricultural fields is a serious environment pollution creator all over India. Rice-Straw is available abundantly after harvest and as a consequence creates disposal problem.According to available sources Paper Industry these days is facing problem of non availability of good quality raw materials. One can identify a suitable technology to convert this Raw-Straw (an agro-residue) into pulp to be used for production of Handmade Paper[1]. This move is not only going to solve environmental problem after the harvest but also going to provide a unique type of raw-material for paper manufacture.

Acetic acid pulping in the presence of sulphuric acid as catalyst has been studied at different pulping conditions.

The effects of change of Catalyst Concentration , Acetic Acid Concentration, Liquor to Straw(dried) Weight Ratio, Temperature and Time of Reactions on the quality of pulp yield were studied.

Experiment with *85 percent* Acetic Acid Concentration , *one percent* Catalyst Concentration, Liquor to Straw Ratio equal to *ten* with Reaction Temperature as *90°C* and Time of Reaction as*180 minutes* show the maximum delignification with good quality of Pulp for Paper making.

The Handmade Papers prepared from this pulp have very high opacity, good brightness and average mechanical properties. The Paper thus produced can be used to make strong carry bags so as to substitute the polythene bags due to environmental reasons.

Introduction

Rice is the major cereal crop of India, covering an area of about 41 million hectares [2], the largest area under any single crop. Accordingly Rice-Straw is abundantly available almost throughout India after the harvest as an agro-residue.

The farmers like to get rid of this residue at the earliest by burning in the open fields in order to prepare the field for the next crop [3].But this open burning produces a significant amount of CO, CO_2, NO_x, suspended emissions which if not controlled act as health hazard.This Agro-Residue being the source of high fibrous lignocellulosic content[4] can be considered as raw material for the manufacture of paper.

The alkaline or Kraft pulping process [5] is by far the most popular chemical pulping process practiced on an industrial scale.Some major difficulties with the Kraft pulping process are: very large capital investment,the emission of reduced forms of sulphur, accompanying odour and higher water usage.Due to these significant problems associated with the current conventional pulping processes, it had been thought worthwhile to move to radically different technologies to obtain the required pulp.

Thus our objectives in this paper is to propose eco-friendly technology of pulping. Acetic acid pulping [6] in the presence of sulphuric acid as catalyst has been studied at different pulping conditions. Rice straw for the study was procured from agricultural fields of Sangrur district of Punjab.

The effects of change of concentration of catalyst, acetic-acid concentration, liquor to straw(dried) weight ratio, temperature and time of reaction were studied. Handmade papers were prepared in laboratory and its mechanical , optical and surface properties were analysed to study its suitability for the purpose.

Review Of Literature

In the year 1950 the Kraft process was very popularly used for new pulp mills.It was the most economical of the major chemical pulping processes and the pulp produced had the best strength properties.

There are number of drawbacks in the Kraft process.This process involves obnoxious odours with even the advanced mills.Capacity of plants based on this process has to be high to be economical.Bleached Kraft pulp mills were targeted by environmentalists because of the use of chlorine,chlorine dioxide or other chlorine containing chemicals.Substitution on chlorine sequence was not easy because of the resistance of the residual lignin in Kraft unbleached pulp towards non chlorine bleaching agents utilized to reach requisite levels of whiteness and cleanliness.

For the reasons stated above, there have been renewed interest in recent years in trying to find alternatives to the Kraft process that will yield pulp with same strengrth but without environmental drawbacks.One of the major areas of activity is 'Organosolov Pulping'.In this process removal of lignin from wood takes place by organic solvents.Processes have been differentiated on the basis of whether they involve (a) Water Hydrolysis at elevated temperature by solvent extraction or co-treatment with solvent and water , (b) Acid-catalyzed solvent treatment, (c) Treatment with Phenolic solvents and (d) Oxidation in the presence of solvents.

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Philosophically, two major commercial approaches have emerged. One centres on isolation of lignin and chemical byproducts in addition to pulp, while the other focuses on pulp only.But the other approach results in much process simplification.

Lignocellulosic component is the major structrul component of woody and non-woody plants such as agricultural residues,grasses and represents a major source of renewable organic matter. Lignocellulose consists of lignin, hemicelluloses and celluloses. Large amount of lignocellulosic waste is generated through forestry and agricultural practices,timber industries and many agro industries and they pose an environmental pollution problem. Sadly, much of the lignocellulosic waste is often disposed off by biomass burning, which is carried out even after formal government restriction and is considered a global phenomenon. However, the huge amounts of residual plant biomass considered as 'waste'can potentially be converted into various different value added products like natural fibres used for paper making, bio-fuels, chemicals, cheap energy sources for fermentation, improved animal feeds and human nutrients.

Keeping in mind the non availability of good quality of raw material and increased emerging environmental issues the need was felt for identification & development of technologies that are suitable for indeginous raw material like Rice-Straw.Here our objective is to propose eco-frindly technology of pulping.Here Organosolov Pulping principle is used following acetic acid pulping in the presence of sulphuric acid as catalyst at different pulping conditions.Rice-Straw for the study was collected from agricultural fields of Sangroor district of Punjab.The effects of concentration of catalyst,acetic acid concentration,liquor to straw(dried) weight ratio,temperature and time of reaction were studied to make good quality Handmade Paper.

Experimental

Experimental part consist of Analysing Rice-Straw as raw material for Pulp making, Study of Effects of Variation of Process parameters on Pulp Yield and Testing of Handmade Paper from the Pulp.

Results & Discussion

Analysis Of Rice-Straw

The determination of 1% NaOH Solubility , Ash and Silica content, Alcohol-Benzene Solubility , Bulk Density , Klason Lignin content , Holocellulose content , Water Solubility and Moisture content of Rice-Straw were performed as per standard TAPPI (Technical Association of Pulp & Paper Industries) methods[9]. The analysis is as per **Table 1.**

Analysis of Rice-Straw was done on samples collected from Sangroor district and the results are as presented in **Table1** . Rice-Straw shows reasonably high percentage of 1% Na OH solubility.This shows the possibilities of ash and silica being dissolved to a large extent. There seems to be large percentage of *amorphous silica* being present in Rice- Straw.

Lignin content is reasonably high. This means delignification for pulp making is a crucial step.High percentage of hollocellulose shows Rice Straw as good raw material for paper making.Alcohol benzene,Hot water and Cold water solubility are quite reasonable which shows pulp formation requires their treatment.

TABLE - 1
ANALYSIS OF RICE-STRAW

Analysis	Avg Value(%)
1% NaOH Solubility	35.75
Ash in rice straw	17.48
Silica in rice straw	13.33
Alcohol benzene solubility of the Raw aterial	10.75
Klason lignin in Rice Straw	17.34
Holocellulose in Rice Straw	55.35
Hot water Solubility	13.49
Cold water Solubility	7.25
Moisture content in Rice-Straw	13.51

Effects Of Variation Of Process Parameters On (Pulp) Yield

The study was as per principles of *organosolov pulping* [7]. This principle involves removal of lignin from wood by organic solvent. In the study the process was catalysed using H_2SO_4.

Following Process variables were studied for Acetic-Acid Delignification catalyzed by Sulphuric Acid [6]:

(i)Acetic acid Concentration(%)
(ii)Catalyst (H_2SO_4*) Concentration(%)*
(iii) Liquor to straw ratio(dried)
(iv) Time of reaction
(v)Temperature

The effect of above Process Variables were studied in terms of pulp yield , kappa number , holocellulose and klason lignin . The study is done with following parameters:

Acetic acid concentration taken as **85%, 75%, 65% and 55%.**

Catalyst percentage (H_2SO_4) taken as **2%, 1.5%, 1.0% and0.5%.**

Liquor to straw ratio taken as **8,10,12 and 14.**

Temperature taken as **90,75,60 and 45 °C.**

The effects of above mentioned parameters are shown in **Table 2**

1.Effects of variation of concentration of acetic acid :

The increase in concentration of acetic acid favors the delignification and provides better pulp with lower lignin left in pulp. *Pulp yield* decreases with increase of acetic acid concentration in liquor due to increase of delignification and solubilization of hemicelluloses in acetic acid (this is very clear from **Table 2)** . But the quality of pulp obtained at higher pulp yield is not suitable for further processing in paper industry due to high kappa number and high residual lignin in pulp. A pulp kappa number equal to 28.5 was obtained at 85 % acetic acid concentration with 1% catalyst concentration at 90 ^{0}C temperature and 180 minutes of reaction time when liquor to straw ratio was maintained at 10. With these process parameters minimum residual lignin content of 5.7% is found in the pulp.

2.Effects of variation of catalyst concentration :

Catalyst (H_2SO_4) concentration of 1%

TABLE- 2

EFFECTS OF PROCESS VARIABLES ON QUALITY OF PULP

Exp (run) No.	*Acetic Acid Conc. (%)*	*Catalyst (H_2SO_4) Conc. (%)*	*Liquor To Straw Ratio*	*Temp. ^0C*	*Time Min.*	*Pulp Yield (%)*	*Pulp Kappa No.*	*Hollo-Cellulose in pulp (%)*	*Klason Lignin in pulp (%)*
1.	*85*	*2*	*10*	*90*	*180*	*65.4*	*71.1*	*68.8*	*14.8*
2	*85*	*1.5*	*10*	*90*	*180*	*61.2*	*51.3*	*71.3*	*10.8*
3	*85*	*1.0*	*10*	*90*	*180*	*52.2*	*28.5*	*77.5*	*5.7*
4	*85*	*0.5*	*10*	*90*	*180*	*56.3*	*42.0*	*72.0*	*8.4*
5	*75*	*1.0*	*10*	*90*	*180*	*53.5*	*32.6*	*75.5*	*6.5*
6	*65*	*1.0*	*10*	*90*	*180*	*55.8*	*34.8*	*72.1*	*7.1*
7	*55*	*1.0*	*10*	*90*	*180*	*57.1*	*37.8*	*72.4*	*7.5*
8	*85*	*1.0*	*12*	*90*	*180*	*58.5*	*41.8*	*71.8*	*8.3*
9	*85*	*1.0*	*14*	*90*	*180*	*60.5*	*44.8*	*72.0*	*8.9*
10	*85*	*1.0*	*8*	*90*	*180*	*63.0*	*60.5*	*70.2*	*12.2*
11	*85*	*1.0*	*10*	*75*	*180*	*57.6*	*39.0*	*73.1*	*8.0*
12	*85*	*1.0*	*10*	*60*	*180*	*62.0*	*53.5*	*71.6*	*10.8*
13	*85*	*1.0*	*10*	*45*	*180*	*63.5*	*68.8*	*69.1*	*13.8*
14	*85*	*1.0*	*10*	*90*	*150*	*54.0*	*32.9*	*74.8*	*6.5*
15	*85*	*1.0*	*10*	*90*	*120*	*55.1*	*36.1*	*72.8*	*7.1*
16	*85*	*1.0*	*10*	*90*	*210*	*51.6*	*28.1*	*82*	*6.2*

provides the best delignification , minimum kappa number and maximum holocellulose percentage in pulp . The detailed effects are shown in **Table2**.

3. Effects of variation of LSR (Liquor to Straw ratio) :

The amount of liquor to straw is an important parameter for uniform and efficient reaction of delignification. The whole mass of Rice-Straw (solid phase) should be in contact with reactant acetic acid which is present in liquid phase. The catalyst is also in liquid phase. The Liquid to Straw Ratio (LSR) was varied from 8 to 14 and best result in terms of quality of pulp was obtained at a LSR of 10.

4. Effects of variation of Temperature :

The increase of temperature of reaction from 45 ^{0}C to 90 ^{0}C has shown the decrease of Klason lignin percentage by slightly more than 50 percent. This is again supported by decrease of kappa number of pulp from nearly 70 to 28. As the constituents get degraded in reaction due to increase in temperature, the overall pulp yield decreases significantly by 18 percent. Detailed observations regarding this effect is shown in **Table 2.**

5. Effects of variation of Time :

Time increase from 120 minutes to 180 minutes results in lowering of lignin percentage in pulp from 7.1 percent to a level of 5.7 percent which shows a decrease of residual lignin by approximately 20 percent . Further increasing the reaction time to 210 minutes, keeping all other parameters constant,lignin percentage in the pulp increases to 6.2 percent.Hence from **Table 2** it is observed that optimum time of reaction is 180 minutes.

Hence after studying variation of various Process parameters as above , the optimum condition of Acetic Acid Pulping is followed which is Acetic Acid Concentration of 85 percent with *one percent* Catalyst Concentration, Liquor to Straw Ratio equal to *ten* with Reaction Temperature at *90 C* and Time of Reaction as *180 minutes.*

Testing Of Paper

Handmade Paper, made from Acetic Acid pulping process at optimized condition as determined by the study in the previous section was subjected to test for various desirable properties:Brightness of Paper,Printing Opacity ,Burst Strength ,Tear Strength and Tensile Strength .Test of these properties were done based on TAPPI procedures.

1.Brightness of Paper

Brightness of paper measured at 457 nano meter wavelength of light in terms of ISO brightness has shown that the pulp has brightness of 26.30 %ISO. Measured brightness of unbleached paper is shown in **Table 3**

2.Printing Opacity of Paper

Printing Opacity of paper is 98.46% as shown in **Table 3**

3.Burst Strength of Paper

Burst strength is one of the most important mechanical properties. It is defined as the pressure applied to paper on a given area which causes burst in paper. Burst Index of paper is derived as burst strength divided by grammage of paper. The average Burst Strength of paper is 0.59kPam^2/g as shown in **Table 3**

4.Tear Strength of Paper

Tear Strength is defined as the energy absorbed in tearing a specified length of paper after giving a initial cut. When tear strength is divided by grammage of paper, it gives tear index which is usually used to measure and compare the strength properties.Average Tear index of paper samples come out to be 3.315mN.m^2/g which is shown in **Table 3**

5.Tensile Strength of Paper

Tensile Strength is measured as the force applied to stretch the paper sample of 15mm width which causes the break in sample. Tensile index is defined as the tensile strength divided by gammage of paper. Tensile index has an average value of 22.76 N.m/g as shown in **Table 3**

TABLE- 3
TESTING OF PAPER

Properties of Handmade Paper	Quantities with units
1.Brightness of Paper	26.30(ISO%)
2.Printing Opacity of Paper	98.46%
3.Burst Strength of Paper	0.59(kPa.m^2 / g)
4. Tear Index of Paper	3.315(mN.m^2/g)
5. Tensile Index of Paper	22.76(N.m/g)

Properties of Handmade Paper as shown in **Table3** was compared with the available values in the literature[7].It was found that values lies within the reasonable limits.

Conclusions

1. Ash and silica percent in rice straw is quite high which is soluble in 1% NaOH quite appreciably. High solubility of Ash and Silica in 1% NaOH shows Rice-Straw having high percentage of amorphous silica.

2. Rice-Straw having 55.35% hollocellulose makes it good raw material for paper manufcture.

3. Best quality of pulp was obtained with kappa number equal to 28.5 at 85 %, acetic acid concentration with 1% catalyst concentration at 90 ^{0}C temperature and 180 minutes of reaction time when liquor to straw ratio was maintained at10.

4. Laboratory Hand Sheet paper was prepared. Paper prepared was tested for Brightness, Printing Opacity, Burst Strength, Tear Strength and Tensile Strength.These properties of Hand Sheet Paper prepared in the laboratory is quite satisfactory for its application as Handmade Paper.

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