Study of Effects of Process Variables of Rice Straw Delignification in Catalyzed acetic Acid Medium at Atmospheric Pressure

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Scarcity of conventional wood based fibrous raw materials for pulp and paper industry is one of the most challenging tasks. On the other side Rice straw burning in agricultural fields is a serious environment pollution problem in India & other countries due to not finding proper utilization. Rice straw is available in abundant quantity in India and other Asian countries, so a suitable technology is required to convert rice straw from a biomass waste to a useful fibrous resource. Acetic acid pulping in the presence of sulphuric acid as catalyst has been studied at different pulping conditions. This pulping method is able to deal with high silica present in rice straw. The pulp obtained retains the 75% 80 % of silica originally present in rice straw. The effects of change of catalyst , acetic acid concentration, liquor to straw weight ratio, temperature and time of reaction were studied . Experiment with one percent catalyst concentration and liquor to straw ratio equal to ten shows the maximum delignification with good quality pulp for paper making. Higher concentration of acetic acid favors the puling process. Effect on holo-cellulose percentage in pulp was also studied for different process parameters. The laboratory hand sheets made from the pulp have very high opacity and average mechanical strength properties.

Key Words: Rice straw, Acetic acid pulping, Catalyst (H_2SO_4), Proximate chemical analysis, Kappa number, Holocellulose, Klason Lignin, Time, Temperature, concentration of acetic acid, Liquor to solid ratio.

INTRODUCTION

The Indian paper industry uses a variety of fibrous raw materials such as wood, bamboo, agro residues and waste paper. Nearly 36% of the paper production comes from the forest based raw material and the remaining from the non-conventional raw materials such as agro residues and waste paper (1). Rice straw is a fibrous lignocellulosic material typical of most agricultural residues; however, it differs from most crop residues in its high content of silicon dioxide (SiO_2). Ash content on a dry weight basis ranges from 13 to 20%, varying according to the state of conservation of the straw after harvest. The ash in rice straw has nearly 75% SiO_2, 10% K_2O, 3% P_2O_5, 3% Fe_2O_3, 1.3% CaO, and smaller amounts of Mg, S, and Na. The potential environmental benefits of diverting rice straw from open-field burning is reduction of air pollutants such as VOC, SOx, NOx, and PM10, and also silica emissions, which are not specifically monitored but can be a health hazard. (2).Annual world rice (Oryzae sativa) production is about 618 million metric tons in year 2005. Asian farmers are contributing nearly 559 million metric tons. India and china produced 130 and 183 million metric tons respectively in 2005. More than 50 countries contribute to this sum with the production of at least 100,000 tons of rice annually (3). For every ton of grain harvested, about 1.35 ton of rice straw remains in the field. Rice straw has a high potential as a source of lignocellulosic biomass because of the high yield of rice straw per hectare. The proportion of recoverable straw depends on the technique of reaping and harvesting (manual or mechanical) and on the condition of the field (wet or dry). About 5.6-6.7 ton per hectare (2.5-3 tons per acre) of dry straw is an average net production. Rice straw was usually disposed of by open-field burning because it is a cheap disposal method (4). At present three-fourth of the crop residue amounting to 70 to 80 million tones of rice straw is disposed of by burning in India.

To facilitate delignification of woody materials, use of organic solvents has been greatly expanded during the past few years (5). The rationale for this work, progress in developing viable commercial processes, differentiating types of processes, and deduction of chemical mechanisms have been studied. Philosophically, two major commercial approaches have emerged. One centers on isolation of lignin and chemical byproducts in addition to pulp, while the other focuses on pulp only concurrent with process simplification. Both will likely have their place in the future. However, the huge amounts of residual plant biomass considered as “waste” can potentially be converted into various different value added products like natural fibers used for paper making, bio-fuels and chemicals (6). A variety of variations on acetic acid pulping have been developed over the years and several new acetic acid based processes are currently under development. Mineral acid catalysts have been utilized to varying degrees of success. Lignin removal and recovery are analyzed. The importance of swelling the lignocellulosic gel is emphasized for lignin removal. The molecular weight characteristics of lignin from acetic acid based pulping of wood are described in relation to liquor composition and degree of delignification. It appears that rapid delignification is associated with removal of large lignin fragments (7). Production of high-purity pulps from Eucalyptus globulus or aspen wood via pulping in organic acid media (Milox or Acetosolv technologies) and totally chlorine free (TCF) bleaching have been studied (8).

Solvent pulping methods can be divided into "uncatalyzed", acid-catalyzed and base-catalyzed processes. The rates of acid-catalyzed processes appear to be governed by the hydrolysis of a-ether bonds in lignin (9). Wood processing in HCl-catalyzed acetic acid media (Acetosolv pulping) provides an efficient way to separate the main fractions of the raw material. In a single step, delignification and hemicellulose degradation are reached with good selectivity. The economic feasibility of this approach depends on

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the recovery of two marketable pulping byproducts: lignin and furfural (10). Organosolv pulping (based on the utilization of organic solvents as delignification media) can be considered as "biomass refining" technologies, since they lead to a solid phase enriched in cellulose and to liquors containing hemicelluloses and lignin-degradation products free from sulfur.

EXPERIMENTAL

MATERIAL

Rice straw was procured from agricultural fields of Sangrur (Punjab). This was washed with water and air dried before packing in air tight plastic containers for analysis and processing. The rice straw was cut into suitable size (1cm 1.2cm) so that we can get uniform reaction during different chemical analysis. The extractive content and other chemical analysis were performed as per standard TAPPI (Technical Association of Pulp & Paper Industries) methods. A number of delignification (pulping) experiments were carried out to study the influence of amount of acetic acid, time of reaction, amount of catalyst H_2SO_4 and liquor to dry matter ratio on delignification rate and chemical characteristics of the rice straw pulp. The manufactured pulp quality was tested by making hand sheet papers and testing different optical and mechanical strength properties.

Table: 1

S.NO..	Analysis	Avg. Value (with variation) for different samples
1.	1% NaOH Solubility (%)	35.75^{+}-2.81
2.	Ash in rice straw (%)	17.48^{+}- 1.30
3.	Silica in rice straw (%)	13.33^{+}- 1.06
4.	Alcohol benzene solubility of the raw material (%)	10.75^{+}- 1.42
5.	Klason lignin in rice straw (%)	17.34^{+}- 0.69
6.	Holocellulose in rice straw (%)	55.35^{+}- 0.68
7.	Hot water solubility (%)	13.49^{+}- 0.43
8.	Cold water solubility (%)	7.25^{+}- 0.45
9.	Moisture content in rice straw (%)	13.51^{+}- 0.98
10.	Bulk density of rice straw (Kg/m^3)	113.8^{+}- 2.8

Analysis of rice straw and pulp produced by acetic acid delignification

Experiments for determination of 1% NaOH Solubility (TAPPI Std. T-212 om-93), ash and silica (TAPPI Std. T-211 om-85), Alcohol Benzene Solubility (TAPPI Std. T-204 om-88), Bulk Density (TAPPI Std. T- 258 om-94), Klason Lignin (TAPPI Std. T-222 om-88), Holo-cellulose (TAPPI Std. T-212 om-75), Water solubility (TAPPI Std. T-207 om-93), Kappa number of pulp (TAPPI Std. T-236 cm-85), Fiber length of pulp by classification (TAPPI Std. T-233 cm-95) were carried out.

Acetic acid delignification of rice straw

Delignification (pulping) reaction of rice Straw was carried out in polyethylene bags at controlled temperature water bath. Acetic acid was used as main chemical and H_2SO_4 was used as catalyst. Each experiment was carried out by taking 100 gm of oven dry rice straw cut into small pieces of 1.0 to 1.2 cm size. After completion of reaction for a given time for that batch, the mass was cooled to 45 to 50 ^{0}C and then filtered out. The crude pulp was obtained above the screen medium and subjected to further processing for analysis.

Process variables of acetic acid Delignification catalyzed by sulphuric acid

a. Acetic acid concentration (%)
b. Catalyst (***H_2SO_4***) concentration (%)
c. Time of reaction
d. Liquor to straw ratio
e. Temperature

Variations of input process variables during delignification reactions

Acetic acid concentration, Catalyst (H_2SO_4) concentration**,** Liquor to straw ratio, temperature and time were varied. Its effect on pulp yield, kappa number, holocellulose and klason lignin were studied**.**

a) Acetic acid concentration has been varied as 85%, 75 %, 65% and 55%.
b) Catalyst percentage has been varied as 2%, 1.5 %, 1.0 % and 0.5%.
c) Liquor to straw ratio has been varied as 8, 10, 12 and 14.
d) Temperature has been varied as 90, 75, 60 and 45 ^{0}C.

Analysis of acetic acid pulp of rice straw

The pulp was analyzed for holocellulose , klason lignin and kappa number and yield percentage. The pulp obtained from acetic acid delignification experiments were selected based on kappa number test for hand sheet paper making and further analysis. Ash and silica percent of selected pulp was determined. Selected pulp outputs were classified in fiber classifier (Bauer Macnett) as per Standard TAPPI procedure.

TESTING OF PAPER

Mechanical Strength properties of Paper made from acetic acid pulp were determined after treating in lab valley beater. Preparation of paper hand-sheet was done by taking 200 gms of O.D. Pulp which was diluted to 2% consistency and beaten in lab valley beater for internal and external fibrillation to 40 ^{0}SR. Paper hand-sheets of 100 gsm were prepared in lab Sheet former. The wet papers were pressed in Lab sheet press and then air dried for 24 hrs. The air dried papers were sealed in polythene bags for analysis of important properties. Paper hand-sheets were conditioned by placing for 3hrs in environment chamber maintained at 25 ^{0}C temperature and 52 % relative humidity. Then the papers were tested for brightness, printing opacity, burst strength (T 403 om-97), tear strength (T 414 om-98) and tensile strength (T 494 om 96) as per std. TAPPI procedures.

RESULTS AND DISCUSSION

Proximate analysis of rice Straw: Proximate analysis of rice straw was done for three different samples. The results are given in Table 1. Ash and silica percent in rice straw is significantly higher than other conventional woody and non woody raw materials being used in pulp and paper industry. Even wheat straw is having nearly half of that present in rice straw. This is a major problem in evaporation and combustion of black

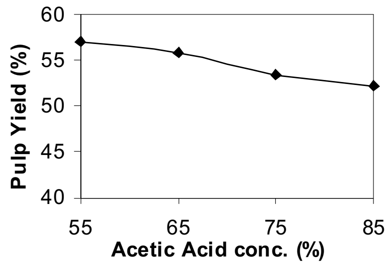

Fig.1: Effect of acetic acid concentration on pulp Yield.

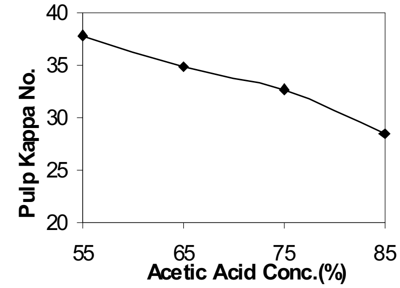

Fig.2: Effect of acetic acid concentration on Kappa No.

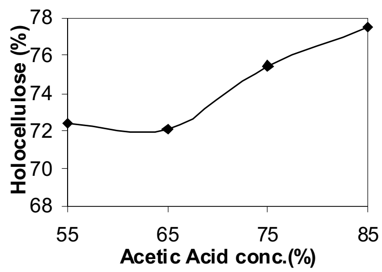

Fig.3: effect of acetic acid conc.on. holocellulose

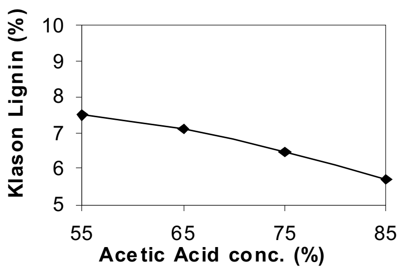

Fig.4: Effect of acetic acid concentration on klason lignin

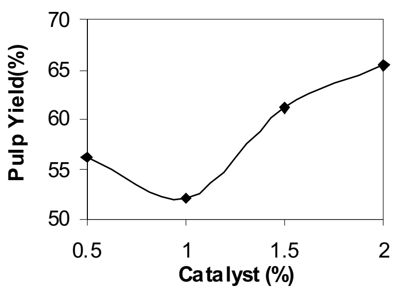

Fig. 5: Effect of catalyst concentration on pulp Yield

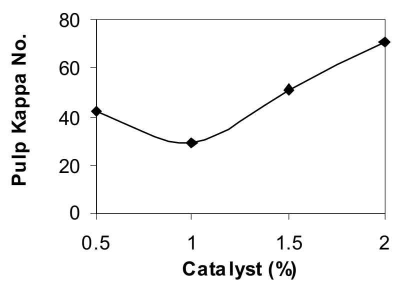

Fig.6: Effect of catalyst concentration on Kappa No.

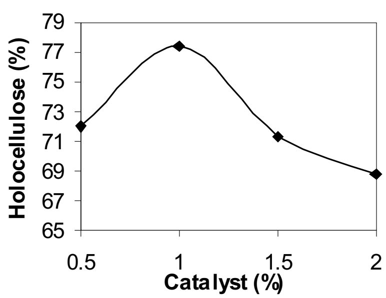

Fig.7: Effect of catalyst concentration on holocellulose

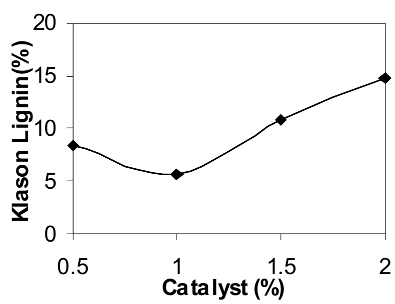

Fig.8: Effect of catalyst concentration on klason lignin

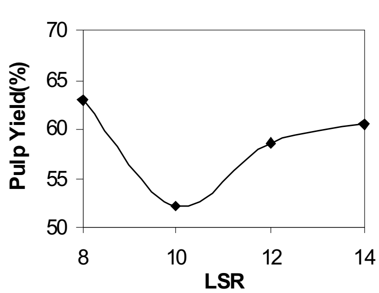

Fig.9: Effect of LSR on pulp yield

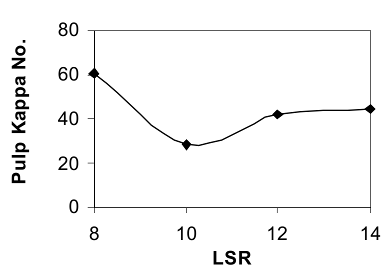

Fig.10: Effect of LSR on pulp Kappa number

liquor obtained by soda or kraft pulping processes. Catalyzed acetic pulping can prove to be a alternative process for use of rice straw in paper industry as cellulosic fiber source due to quite lower dissolving of silica in spent liquor

Effects of variation of process parameters on product (pulp) yield & other important characteristics

Effects of variation of concentration of acetic acid

The increase in concentration of acetic acid favors the delignification and provides better quality pulp with lower lignin content. Pulp yield decreases with increase of acetic acid concentration in liquor due to increase of delignification and solubilization of hemicelluloses in acetic acid. 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 residual lignin in pulp. A pulp kappa number equal to 28 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. The detailed effects are shown in graphs given in Figure.1. To 4.

Effects of variation of catalyst concentration: Catalyst (H_2SO_4) concentration of 1% provides the best delignification, minimum kappa number and maximum holocellulose percentage in pulp with 5.7 percent Residual lignin. The detailed effects are shown in graphs given in Figure 5. To 8.

Effects of variation of LSR (Liquor to straw ratio): The amount of liquor to straw is an important parameter for uniform and efficient delignification reaction. The whole mass of rice straw (solid phase) should be in contact of another reactant acetic acid which is present in liquid phase. Again the catalyst is in liquid phase only. The LSR was varied from 8 to 14 and best result was obtained at a LSR equal to 10. The detailed effects are shown in graphs given in fig.9 To 12.

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

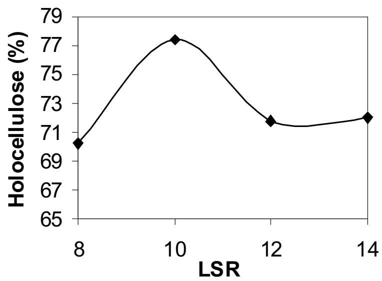

Fig.11: Effect of of LSR on holocellulose

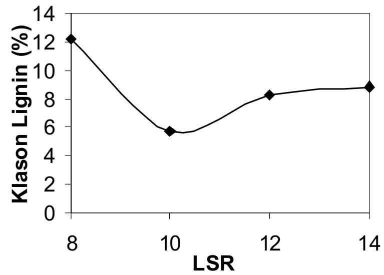

Fig.12: Effect of of LSR on klason lignin

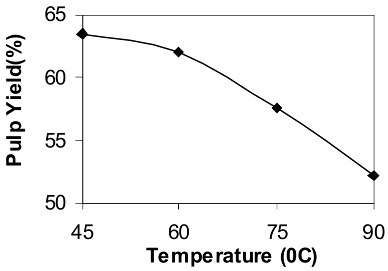

Fig.13: Effect of reaction temperature on pulp yield

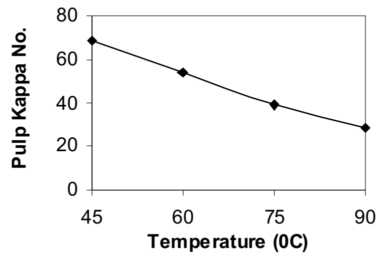

Fig.14: Effect of reaction temperature on pulp kappa No.

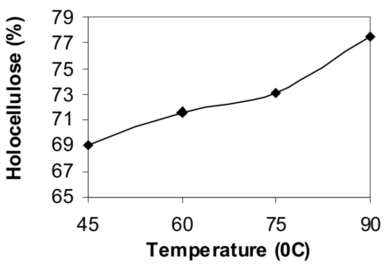

Fig.15: Effect of reaction temperature on holocellulose

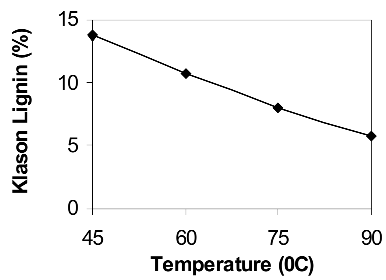

Fig.16: Effect of reaction temperature on klason lignin

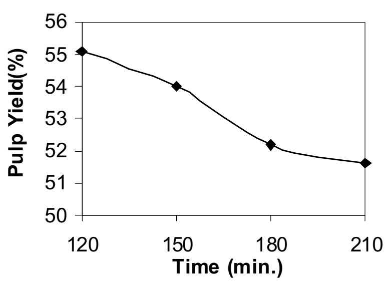

Fig.17: Effect of time of reaction on pulp yield

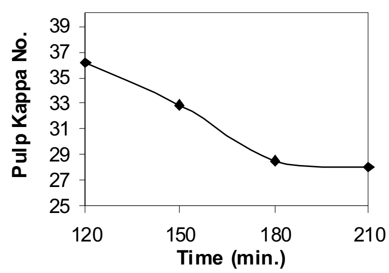

Fig.18: Effect of time of reaction on pulp kappa number

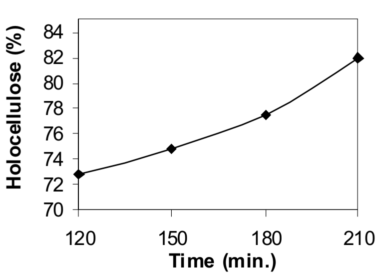

Fig.19: Effect of time of reaction on pulp holocellulose

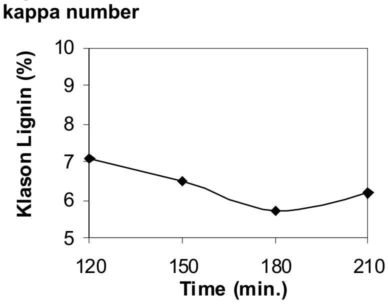

Fig.20: Effect of time of reaction on pulp klason lignin

decrease of kappa number of pulp from nearly 70 to 28. As the constituents get degraded in reaction, the overall yield decreases significantly by 18 percent. The detailed effects are shown in graphs given in Figure 13 To 16.

Effects of variation of time : Reaction time increase leads to completion of reaction. Time increase up to 180 minutes results in lowering of lignin percentage in pulp to a level of 5.7 percent from 17.3 percent which shows a decrease of 67 percent. Further increase of time does not help in delignification. The change of kappa number also shows the similar trends. Detailed effects of time variation are shown in graphs given in Figure 17 To 20.

Mechanical Strength properties of Paper hand sheet from acetic acid pulp:

Mechanical Strength properties were determined for pulp obtained by acetic acid pulping after treating in lab valley beater . The beaten pulp was having 40 ^{0}SR. 100 gsm paper was made and tested for burst strength, tear strength and tensile strength. Burst index of paper samples varied from 0.52 to 0.65 kPa.m^2 /g . The average value of 0.59 kPa.m^2 /g is suitable for Maplitho grade or newsprint paper. Tear index of paper samples varied from 3.25 to 3.38 mN.m^2 /g . The average value of 3.33 mN.m^2 /g is good for average grades of writing and printing paper. Tensile index has values in between 22 to 23.90 N.m /g and The average value is 22.99 N.m /g. The lower value of tensile, tear and burst index is with nearly 15 % of fillers content in paper. So it is quite good considering such a heavy filler loading.

Further addition of 5-10% long fiber (as in usual practice in paper industries using short fiber pulp) in rice straw based short fiber stock will enhance all the strength properties significantly and make it suitable for good quality writing and printing paper due to better bonding in between fibers.

Optical properties of Paper from acetic acid pulp:

Brightness of paper measured at 457 nano meter wavelength of light in terms of ISO brightness has shown that the pulp has brightness in between 25.38 to 26.81 % ISO. This is good and can be easily bleached to 80 85 % ISO brightness by conventional bleaching sequences.

Opacity of paper made of bleached pulp is varying in between 97.9 to 98.8 %. This is very high and makes the paper very good for writing and printing purpose as readability improves with increase of opacity.

CONCLUSIONS

The following conclusions may be drawn from this research project:

1. Rice straw has a good potential to be an alternative raw material for paper making and may prove to be a major source of natural cellulosic fibers for lower and medium quality writing and printing grades of paper.

2. Very high ash percent (17.4 %) & silica percent (13.3 %) of rice straw in comparison to other conventional raw materials makes it very difficult to be handled by conventional chemical pulping (Soda or Kraft) processes.

3. The lignin percent (17.3%) in rice straw is lower than most of the conventional raw materials so it is easier to delignify.

4. The increase in concentration of acetic acid favors the delignification and provides better quality pulp with lower Kappa No. Pulp yield decreases with increase of acetic acid concentration in liquor due to increase of delignification and solubilization of hemicelluloses.

5. Catalyst (H_2SO_4) concentration of 1% provides the best delignification, minimum kappa number and maximum holocellulose percentage in pulp.

6. The liquor to straw ratio should be maintained at 10 for better results of delignification.

7. The increase of temperature of reaction leads to decrease of Klason lignin percentage & decrease of kappa number of pulp significantly.

8. Reaction time increase provides increase of delignification but time increase after 180 minutes is not adding any significant positive change. So three hours time is optimum.

9. Unlike soda or kraft pulping, the amount of ash and silica retained in the pulp are very high. As ash percent and silica percent in pulp are 15.5 and 13.8 respectively.

10. Weight average fiber length of acetic acid pulp of rice straw is 0.89 mm which is good enough for manufacturing lower and average grade of papers.

11. Brightness of unbleached acetic acid pulp hand-sheet was 26.3 % ISO which is average.

12. Printing opacity of acetic acid delignified pulp was very high (above 98%), which provides very good quality for writing and printing grades of paper. This very high opacity is because of inherent ash present in pulp.

13. Burst and Tensile index were lower due retention of higher percent of silica but tear strength is good.

14. The separation of components from spent liquor is easy. Acetic acid can be easily recovered by fractional distillation to be used in next pulping processes.
So this process can provide a breakthrough for utilization of rice straw as a natural fiber resource for paper industries.

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