# "Preliminary Assessment Of The Lignocellulosic Raw Material - Fibrous (Cellulose) And Non-Fibrous (Lignin And Hemicellulose)"

**Sheetal** [*]**, Dr Sanjay Naithani** [**]

[*] Research Scholar, Chemistry Division, (Centre  for advanced studies in chemistry of forest product ), Forest Research Institute
P.O. New Forest, Dehradun
[**] Scientist,Cellulose and Paper Division, Forest Research Institute, P.O. New Forest, Dehradun

*Abstract-* The knowledge of the chemical composition of the prospective raw material under study is one of the essential prerequisites for characterization of effluent.

Since the present work deals with the investigation carried out an agricultural residue(wheat straw) the proximate chemical analysis have been carried out to compare the structural components of straw with hardwood with particular reference to the components which are of significant value in assessing the paper making potential on chemical basis.

## I. INTRODUCTION

The determination of proximate chemical analysis is just preliminary assessment of the lignocellulosic raw material in terms of its fibrous (cellulose) and non-fibrous (lignin and hemicellulose) which undergoes chemical reaction during the cellulose extraction and subsequent bleaching chemical treatment. The condition employed for pulping, bleaching and the consumption of chemical depend upon the nature and chemical composition of the raw material used.

Bagasse is the fibrous residue remaining after sugarcane or sorghum stalks are crushed to extract their juice[1] and is currently used as a renewable resource in the manufacture of pulp and paper products and building materials India is one of the leading sugar cane producing country and bagasse is by product of the sugar industry and it is renewable fibre resource. It is observed that nearly 19 million tons of the bagasse being produced in the organized sector is adequate to produce 3 million tons of paper form pulp[2]. As sugarcane is grown in most part of the country the sustained availability of bagasse to paper can be ensured. Further, with high density baling technology available the transportation should not be a problem. Thus, the abundance and easy transportation make bagasse an attractive fiber resource for paper industry.

Around 5%-10% of paper production worldwide is produced from agricultural crop, valuing agricultural paper production between $5 billion and $10 billion[3]. Due to the ease with which bagasse can be chemically pulped, bagasse requires less bleaching chemicals than wood pulp to achieve a bright, white sheet of paper. The fibers vary in length depending on the country but the typically about 1.3 mm to 1.7 mm long. Bagasse fibers are well suited for tissue, corrugating medium, newsprint, and writing paper[4,5]

The significant of each analysis is discussed below:

### 2.1.1 Ash Content:

Ash content include various inorganic salts of sodium, calcium, potassium, silica, iron, sulfates and chlorides etc. The agricultural residues are characterized by high ash content (3-18%) [8], whereas the quantity of ash in wood is very low (0.2 to 0.8%). The high ash content in agricultural residues is mainly due to presence of silica. The silica present in the raw material enters the spent liquor during pulping and poses many problems in the chemical recovery process[9].

During concentration of the spent liquor, the silica forms a layer on the heat transform surface of the evaporator and reduce the heat transfer efficiency[10]. The entry of chlorides into the system affects the thermal behaviour of the spent liquor,[11] by increasing the eutectic point.

### 2.1.2 Solubility in Boiling Water:

Hot water solubility determination is a measure soluble component like starch, resins, pectin, low molecular weight polysaccharides and other extractives. This measurement helps in assessing the chemical requirements during pulping.

### 2.1.3 One Tenth Normal (N/10) Sodium Hydroxide Solubility:

This determination is a most informative parameter to assess the physicochemical nature of the raw material. It also gives an idea about the microbial decomposition /degradation of a particular raw material. The degradation of raw material is due to low molecular weight components[12].

### 2.1.4 Alcohol- Benzene Solubility:

Alcohol-benzene solubility constitutes the determination of waxes, fats, resinous matter and certain other low molecular weight soluble components. The ethanol-benzene is the most suitable combination for solubilizing majority of the components soluble in organic solvents since no single organic solvent is capable of removing all these substance and different solvents remove different combinations.

### 2.1.5 Lignin:

Lignin is an amorphous three -dimensional complex polymer made up of phenylpropane units. It is binding material of fibers and imparts rigidity to the plants tissue. Estimation of lignin content in dusty samples is important and helps in arriving at conditions required for delignification during pulping. The lignin content of the spent pulping liquor is dependent upon the lignin content of the raw material and amount of lignin dissolved during pulping. Lignin is isolated from extractive free dust as acid insoluble residue after hydrolysis of polysaccharides with in 72% sulfuric acid ($H_2SO_4$). The lignin determination by the method called "Klason Lignin", since Klason was the first person to carry out the reaction of wood dust with 72% of $H_2SO_4$ for quantitative determination of lignin [13].

## 2.1.6 Holocellulose:

Cellulose and hemicellulose are collectively termed as holocellulose. It constitutes nearly three fourth of the fibrous material. Holocellulose includes (i) alkali resistant alpha cellulose (ii) the water-soluble polysaccharides and (iii) the group of water insoluble and strong alkali, soluble hemicellulose portion is readily hydrolyzed by acid as compared to cellulose [14].

Cellulose is the major component of cell wall of wood fibers. It is the basic ingredient which is used in paper and rayon making. Cellulose is a linear polysaccharide of sufficient chain length and is insoluble in water or dilute alkali or acid room temperature. Cellulose constitutes 40-50% by weight of wood. On hydrolysis it forms glucose. Its chemical formula is $(C_6H_{10}O_5)n$, the value of n varies from 800 to 1500 and the building block is a hexose sugar (glucose). The glucose unit are linked through 1-4 β-D glucosidic linkage.

Hemicellulose are the principle non-cellulosic polysaccharide present in plants tissue. These are deposited in the interface of the cellulose fiber in the primary as well as secondary cell of the plant materials. These are low molecular weight linear chain polymers, with degree of polymerization (DP) value of $=100\text{-}200$ [14]. There can be extracted by cold dilute alkalies from hemicellulose. The total hemicellulose content of wood varies between 15-35% major portion of hemicellulose contain pentosans. A low pentosan containing raw material is more suitable for paper grade pulp. Increased proportion of hemicellulose leads to higher proportion of carbohydrates derived acids in spent liquor and also affect the pulp and spent liquor properties.

10 kg of each sample (air dried) of rice straw and bagasse (whole bagasse and depithed bagasse) was collected from Mill A (Uttarakhand) and Mill B (Uttar Pradesh). Then raw material was dried in air and kept in polythene bag for maintain uniform dryness. The sample were converted into dust. The dust passing through 40 mesh and retained on 60 mesh was analysed for chemical composition.

## 2.2 EXPRIMENTAL
## 2.2.1 Preparation of Saw Dust of Raw Material:

For determining the chemical composition of the different components of the raw material, dust was prepared as per the method given below:

Sample of rice straw and bagasse was taken and a part of these raw material weighing nearly 400g was used the dust preparation in the Wiley Milling Machine. The material retained on 40 mesh was again converted into dust so that all the 400g of the raw material was converted into dust passing through 40 mesh screen and retained on 80 mesh as per the standard described in TAPPI method[15].

## 2.2.2 Determination of ash Content:

The dust of rice straw and bagasse sample (2.00 g o.d. basic) was taken in a pre-weighed platinum crucible and ignited at $575 \pm 25$®C in a muffle furnace to obtain the ash. The ignition was continued till constant weights were obtained the ash content was calculated as follows:

$$\text{Ash content (\%)} = \frac{B \times 100}{A}$$

Where : A is the o.d weight of test specimen
B is the weight of residue left after ignition
The ash was divided into different parts for the estimation of different elements.

## 2.2.3 Determination of Silica[15,16]

Silica was determined by using the ash obtained as above (Determination of ash content), known quality of the ash was baked in a beaker with dil hydrochloric acid(HCL). After baking the silicilic acid gel was filtered on ash-less whatman filter paper and washed thoroughly till free of chlorides. After washing the residue was ignited at 600®C in pre weighed platinum crucible and weighted after attaining constant weight. The residue of silica along-with other inorganics was treated with mixture of conc.$H_2SO_4$ and hydrofluoric acid (HF). The platinum crucible was slowly heated on sand bath to expel excess of $H_2SO_4$. Silica with HF forms silicon tetra fluoride, which is volatite on heating. The crucible was weight after igniting at 850®C. The loss in weight was expressed as silica in terms of percentage silica[17].

Silica was calculated as follows:

$$\text{Silica (\%) w/w} = \frac{A - B}{W} \times 100$$

Where,
A is the weight of residue at 600® C
B is the weight of residue left after 800® C
W is the O.D weight of sample

## 2.2.4 Estimation of Calcium, Potassium [18]:

The filtrate obtained after treatment of ash with HCL was used for analysis of calcium(Ca ) and potassium (K)by Flame photometer. Flame photometer is based on the principle that for an atom to emit light, it has to be excited above its ground state by supplying enough energy to move one electron to high energy level orbit. The wavelength for potassium and calcium are 767 nm and 622nm respectively and filters corresponding to these wavelengths were employed for determination of individual element. Standard of Ca, K in the range varying from 1-10 ppm were employed for calibration.

**2.2.5 Determination of Hot Water Solubility [19]:**

Sample dust (2.00-g o.d basis) was taken in an Erlenmeyer Flask (250ml) fitted with a reflex condenser and 100 ml of distilled water was added to it. The flask was kept over a boiling water bath and refluxed continuously for 3 hours, making certain that the water levels is maintained constant . After 3 hours the contents of the flask were filtered into a crucible, washed thoroughly with hot distilled water and dried to constant weight at 105±3®C in an over.

Hot water solubility was calculated as follows:

$$\text{Hot water solubility, (\%)} = \frac{(A-B) \times 100}{A}$$

A is o.d weight of test specimen before extraction
B is o.d weight of test specimen after extraction

**2.2.6 Determination of One Tenth Normal Sodium Hydroxide Solubility[20]:**

Sample dust of both the raw material rice material rice straw and bagasse (2.00 g o.d basis) was placed in 250 ml concial flask and 100 ml of 0.1 N NaOH solution was added to it. The contents were boiled under reflux for one hour. After 1 hour, the contents of the flask were filtered into a crucible. The residue was further washed with hot distilled water followed by 50ml of 10% acetic acid and finally with hot distilled water. The crucible with content was dried in oven at 105±2®C till constant weight was obtained.

NaOH Solubility was calculated as follows:

$$\text{N/10 NaOH solubility (\%)} = \frac{(A-B) \times 100}{A}$$

Where,
A is o.d weight of test specimen before extraction
B is o.d weight of test specimen after extraction

**2.2.7 Alcohol -Benzene Solubility[21]:**

It is a measure of waxes, fats, resins and other ether insoluble components. Dust sample (2.00 g o.d. basis) was taken in a pre- weighed porous thimble which was placed in a soxhlet apparatus. The extraction was carried out with 150 ml of the solvent mixture containing 1 volume of ethanol (95% ethanol) and 2 volume of benzene for 6 to 8 hours, so that 24 extraction cycle were completed. After extraction the thimble was removed and dried in an oven at 105±2 ®C to a constant weight.

Alcohol Benzene solubility was determined as follows:

$$\text{Alcohol – Benzene solubility (\%)} = \frac{(A-B) \times 100}{A}$$

Where,
A is o.d weight is test specimen before extraction.
B is o.d weight of test specimen after extraction

**2.2.8 Estimation of Klason Lignin [22]:**

The alcohol-benzene extracted free dust sample (2.00 g o.d basis) were placed in a clean glass mortar to wich 15.00 ml of 72% sulfuric acid was added gradually in small increments. While adding the acid, the dust of both the raw material was stirred and macerated continuously with glass rod. After 2 hours the material was transferred to one litre conical flask and the acid concertation was brought down to 3% by adding distilled water (575 ml).The contents of the flask were then boiled for 4 hours to accomplish the complete hydrolysis of carbohydrates. During this period , the total volume in the flask was maintained constant by frequent addition of hot distilled water.

After 4 hours the content were filtered into a crucible and thoroughly with hot distilled water until acid free. The crucible was dried to a constant weight at 105±2®C in an oven.
The lignin was calculated as follows:

$$\text{Klason Lignin contents (\%)} = \frac{A \times 100}{W}$$

Where,
A is the o.d weight of lignin
W is the o.d weight of test specimen

**2.2.9 Determination of Holocellulose[23]:**

The basic principle of this method is selective is selective dissolution of lignin by acid chlorite treatment. Extractive free dust samples of rice straw and bagasse (2.0 g o.d basis)was placed in 500-ml conical flask containing 160 ml distilled distilled water. The dust samples were then treated with sodium chlorite(1.5 g)and glacial acetic acid (0.5ml). The contents were placed on a hot water bath maintained at 75-80®C. After 1 hour, sodium chlorite (1.5g) and glacial acetic acid (0.5ml) were again added. The process was repeated till the sample residue became white. The contents were then filtered into a crucible and wasted with distilled water followed by acetone. The crucible was dried to a constant weight in an oven at 105±2®C.
Holocellulose was calculated as follows:

$$\text{Holocellulose (\%)} = \frac{A \times 100}{W}$$

Where,
A is the o.d weight of holocellulose
W is the o.d weight of the test specimen

Table -1 Proximate Chemical Analysis of Bagasse Mill A and Mill B

| Particulars | Mill A | | Mill B | |
|---|---|---|---|---|
| | Whole Bagasse | Depithed Bagasse | Whole Bagasse | Depithed Bagasse |

| | | | | |
|---|---|---|---|---|
| Ash, (%) w\w | 2.20 | 1.80 | 2.16 | 1.73 |
| Sodium, (%) w\w | 0.012 | 0.012 | 0.019 | 0.018 |
| Calcium, (%) w\w | 0.43 | 0.40 | 0.36 | 0.27 |
| Potassium, (%) w\w | 0.61 | 0.57 | 0.59 | 0.55 |
| Silica, (%) w\w | 1.11 | 0.69 | 1.27 | 0.83 |
| N\10 NaOH solubility,(%) w\w | 30.3 | 29.6 | 31.6 | 30.40 |
| Hot water solubility, (%)w\w | 6.4 | 6.1 | 6.40 | 6.07 |
| Alcohol-benzene solubility,(%) w\w | 2.8 | 2.5 | 2.80 | 2.44 |
| Holocellulose, (%) w\w | 68.2 | 72.0 | 68.31 | 71.77 |
| Klason Lignin,(%)w/w | 21.9 | 20.1 | 21.11 | 19.98 |

All values expressed on basis of O.D. raw material

Table-2 Proximate Chemical Analysis of Wheat Straw Mill A and Mill B

| Particulars | Mill A | Mill B |
|---|---|---|
| Ash, (%) w\w | 6.40 | 5.91 |
| Silica, (%) w\w | 6.20 | 5.85 |
| Calcium, (%) w\w | 0.22 | 0.21 |
| Potassium, (%) w\w | 0.89 | 0.87 |

| | | |
|---|---|---|
| Pentosan, (%) w\w | 18.90 | 18.30 |
| Klason Lignin, (%) w\w | 12.80 | 13.10 |
| Holocellulose, (%) w\w | 62.40 | 61.63 |
| Alcohol-benzene solubility, (%) w\w | 1.10 | 1.1 |
| N\10 NaOH solubility, (%) w\w | 48.00 | 46.89 |
| Hot water solubility, (%) w\w | 19.20 | 19.45 |

All values expressed on basis of O.D. raw material.

### 2.3 Result and Discussion:

Result of proximate chemical analysis of bagasse (whole bagasse and depithed bagasse) and rice straw are shown in table 1 and 2. The ash content indicates the mineral constituents present in the raw material in the form of sodium, potassium, calcium, silica and iron etc. The ash contents in rice straw collected from both mill was high as compared to bagasse. There was marginal difference in value of ash between the raw material obtained from the two mills. The ash content in whole bagasse was higher than depithed bagasse. The reason is that during depithing, the ash passes with the pith. The high amount of calcium and sodium in both materials could be from the fertilization through adsorption by the plant cells. The silica content, the main characteristic of agro fibre was higher in wheat straw than bagasse. Silica constitutes the major portion of the ash content, silica enters in the spent liquor during pulping and poses several problems in pulping and recovery cycles.

The hot water solubility was higher in bagasse as compared to rice straw indicating the pressure of low molecular weight carbohydrates and water-soluble extractives. Alcohol- benzene solubility as indicated of extraneous substance was also high in whole bagasse. The alcohol benzene solubility was low in case of rice straw.

One tenth normal alkali solubility showing the amount of short chain hemicellulose[24] and probabilities of decay was higher in rice straw than bagasse. This shows that normal storage of rice straw leads to considerable deterioration of the raw material.

There was not much variation in Klason lignin content between rise straw collected from two mills. Klason lignin was higher in case of bagasse, the whole bagasse was high in lignin content than depithed bagasse. Holocellulose content in bagasse

was higher. Depithed bagasse had higher percentage of holocellulose, atmospheric conditions lead to the appreciable degradation of holocellulose.

From the result depicted in table-1 and table-2 ,it is clear that the raw material content form both mills did not vary much in terms of chemical composition.

## References

[1]   Bagasse- Britannica Online Encyclopedia.

[2]   Rangan S.G., 1986. IPPTA 23 (4):2

[3]   Rainey (2009) A Study into the permeablility and compressibility properties of bassage pilp, Ph.D thesis, Queensland University of Technology.

[4]   Covey , Rainey and shore (2006) The potential for bagasse pulping in Australia, Appita J.59:1 17-22

[5]   Kellomaki, Seppo "4" (in english) Forest Resources and Sustainable ManagementPapermaking Science and Technology2Helsinki, Finlandp.179ISBN952-5216-02-0.

[6]   Mahajan, Sushma. 1998. Up-gradation of wheat straw and rice straw for pulp and papermaking. IPPTA, Vol.10,No.3, Sept.

[7]   Veeramani, H. Non wood plant fiber pulping-Tappi Progress report No. 9,p.97.

[8]   Patel, J.R., Angadiyavar, C.S., Rao, Y.S., Non wood plant fiber pulping – Tappi Progress report, No.15, p.80-83.

[9]   Panda, A.1962.Indian Pulp and Paper , XVI:7.

[10]   Tandon, R.,Gupta, A., Kulkarni , A.G. and Panda, A.1989. Proceeding of international seminar and workshop on destination, India, p.26.

[11]   Milanova, E.1988.J.P.P.S.14(4):J:95.

[12]   Anderson, O.E., 1937. Paper Trade Journal 104(6):42

[13]   Klason, P.Arvik.Kemi,1906.3:17.

[14]   Soderhjelm, L. Communication from the Finnish Pulp and Paper Research Institute, Helsinki.1988.

[15]   Ash in wood official standard, 1976. T-156, Tappi, Atlanta.

[16]   International standard of CPPRI for testing of Pulp and paper, Saharanpur, India.

[17]   Benedetti, P.A. an introduction to microtechniques of inorganic analysis. John Wiley & Sons, New York.

[18]   Dean, J.A. and Rains, T.C.1969. Flame Emission and Atomic Absorption spectrophotometry, Vol.1.

[19]   Water solubles in wood. Official standard, 1975. T-207, Tappi, Atlanta.

[20]   Solubility of wood in boiling tenth normal sodium hydroxide 1958. P.5m-61, Appita, Melbourne.

[21]   Alcohol benzene solubles in wood and pulp official standards 1976. T-204, Tappi, Atlanta.

[22]   Acid insoluble lignin in wood and pulp official standard 1974. T-222, Tappi, Atlanta.

[23]   Wise, E.L.1946. Paper Trade Journal, 122,35

[24]   Morgan , H.W.1931. Paper Trade J.92(15):51.

## Authors

**First Author** – Sheetal, Research Scholar, Chemistry Division (Centre  for advanced studies in chemistry of forest product ) Forest Research Institute, P.O. New Forest, Dehradun Mobile: 9411112290, E mail: drgskashyap@gmail.com
**Second Author** – Dr Sanjay Naithani, Scientist, Cellulose and Paper Division, Forest Research Institute, P.O. New Forest Dehradun