

1 **Modification of Rice Straw Pulp by Calcium Carbonate/ Microcrystalline Cellulose**

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3 **Abstract:** Rice straw is a locally available lignocellulosic material . It is pretreated with
 4 water for 48 hours at room temperature then cooked by 5% NaOH at atmospheric
 5 pressure. The structure and mechanical properties of produced pulp was investigated.
 6 Hydrogen peroxide bleaching agent was applied to high yield pulp to enhance brightness
 7 level in a single stage process in the presence of sodium hydroxide and magnisium
 8 sulphate. Microcrystalline cellulose (MCC) was prepared from alpha cellulose of rice
 9 straw pulp bleached using 2% hydrogen peroxide solution, so that it is characterized by
 10 45.5% crystallinity and nano size. Microcrystallin cellulose was added to unbleached
 11 pulp as filler in presence of calcium carbonate. Optical properties, water permeability and
 12 air permeability of filled pulp show improvements in the presence of microcrystallin
 13 cellulose filler compared to unfilled pulp.

14 Key words: Rice straw, microcrystalline cellulose, water permeability, air permeability.

15 1.Introduction

16 Many cereal straws, particularly rice straw, have been used as raw materials for paper
 17 production. Non-wood raw materials account for 5-7% of the total pulp and paper
 18 production worldwide (Navaee-Ardeh et al. 2004). Hydrogen peroxide is widely used as
 19 an environmentally friendly bleaching agent of paper-making industry. Bleaching of pulp
 20 with alkaline hydrogen peroxide resulted in conversion of conjugated chromophoric
 21 groups associated with lignin structure to carboxylic acids and other degradation products
 22 (Gierer et al 1982). Previous studies also reported that the number of charged groups
 23 increases in peroxide bleaching and/or alkaline treatment of mechanical pulps due to
 24 alkaline hydrolysis of ester groups in the pulps (Sundberg and Praaanoovich 1999).
 25 Cellulose is a classical example of a renewable and biodegradable structural plant
 26 polymer which can be processed into whisker-like micro fibrils (Abraham et al. 2011;
 27 Eichhorn et al. 2011). Recently, researchers reported the extraction of cellulose fibers
 28 from rice husk by alkali and bleaching treatments, which were subsequently converted to
 29 nanocrystals using a sulfuric acid (H₂SO₄) hydrolysis treatment (Johar, Ahmad, &
 30 Dufresne, 2012). Isolation of microcrystalline cellulose has been carried out from jute
 31 cellulose by using the same acid hydrolysis (H₂SO₄) approach (Jahan & Saeed, 2011).
 32 The hydrolysis of cellulose to obtain MCC can be accomplished using enzymes or
 33 microorganisms. Although enzymatic methods are desirable because glucose, a useful by-
 34 product, is created, these methods are more expensive and create MCC products having a
 35 lower crystallinity. Thus, acid hydrolysis is the conventional method of choice for
 36 manufacturing MCC (Hanna et al. 2001).

37 Microcrystallin cellulose could be produced from alpha cellulose obtained from wood
 38 pulp by hydrolysis with hydrochloric or sulphuric acid. Microcrystallin cellulose could
 39 be also produced in an autoclave from ground lignocellulosic materials by heating with
 40 steam at 205- 250 °C for 15 minutes, followed by bleaching of cellulose with hydrogen

peroxide and finally hydrolyzing cellulose with mineral acids.(Ilindra & Dhake 2008). Microcrystalline cellulose (MCC) is widely used as a filler and a binder for wet granulation, direct compression tableting and as a filler for hard gelatin capsules. It has low chemical reactivity combined with excellent compactibility at low pressures. (Michael & Girard 1998).

The choice of fillers usually takes into consideration primarily the desired performance in a specific paper grade, the mill internal situation, logistical possibilities and consequences, the general availability of the product, and the costs, including the external and internal logistics. Optimizing one type of filler for a specific paper grade usually results in a compromise between the obtainable properties with this filler. In cases where one single pigment does not meet all the requirements, filler combinations are applied. There is a continuous trend towards fully or partially replacing specialty pigments by regular or modified regular fillers (Holik et al 2006). The brightness of the regular filler kaolin is distinctly lower than most CaCO_3 based fillers. For this reason, in recent decades, kaolin has been largely globally replaced by CaCO_3 fillers in wood-free uncoated papers (Holik et al 2006). Rice straw is an available, local fibrous material produced in large quantities every year. Recently, it is used for paper making or as a filler in wood plastic composites industry. In the present investigation, it is used for the production of micro crystalline cellulose from rice straw pulp by hydrolysis using hydrochloric acid. The aim of the present work is to produce rice straw pulp from rice straw at low temperature and at atmospheric pressure. The pulp was used in paper making and preparing microcrystalline cellulose to apply it as a filler in paper making.

2. Experimental:

2.1 Pulping

Rice straw was used as a raw material in this research. It is cut into pieces of approximately 3 cm length. Rice straw was pretreated through soaking in water at room temperature for two days. After water was peeled, straw was cooked using 5% sodium hydroxide based on oven dry weight of raw material. The condition of pulping was as follows:

Liquor ratio: 1:8, pulping time: 2 hours, pulping temperature: 100 °C at atmospheric pressure. After the required time, pulp was allowed to cool, filtered, and washed by water till neutrality. Pulp yield was calculated using oven dry weight.

2.2 Bleaching

Hydrogen peroxide: 40 wt% aqueous solution of commercially available purity. All experiments on pulp bleaching were made in plastic bags placed in a thermostatic shaker water bath.

The conditions of bleaching were as follows: pulp concentration – 10%, NaOH 2% on o.d. pulp, H_2O_2 charges were 1, 2, 4%, temperature 80°C, treatment time 90 mins., and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (0.6% on o.d. pulp) stabilizer was dosed into an alkaline medium (pH 9).

After bleaching, the pulps were washed with water to neutral condition and dried at room temperature. Magnesium sulfate was used in the peroxide stage in order to prevent radical degradation reactions of carbohydrates since this salt is reported as extremely efficient at reducing the rate of peroxide decomposition (Lapierre et al. 2003; Ashori et al., 2006). The optical properties of unbleached control, bleached and filled pulp presented in brightness and opacity were measured using Hunterlab color difference meter D25-2. Calcium carbonate assay 99. 5% obtained from SRL. CO. and the prepared MCC were added to unbleached rice straw pulp as fillers in 10% based on o.d pulp before paper making by 1 hour.

2.3 Tests

Alpha cellulose of unbleached and bleached pulp was estimated using 17.5% sodium hydroxide solution. Hand-made paper sheets of basis weight 80g/m² were prepared using Tappi Standard Method 414 while T-211 for ash. Water Permeability, air Permeability, bursting resistance were measured using BS 6906, ASTM D 737, ASTM D 3786 Tayousiki Japan methods respectively.

2.4 Microcrystalline cellulose preparation and characterization

2.5 g alpha cellulose of pulp (bleached using 2% H₂O₂) was added to 50 ml 2.5 N hydrochloric acid. This mixture was heated at 80°C for 15 minutes. It was allowed to cool at 50°C and centrifuged using magnetic stirrer for 10 minutes. The product was filtered and washed by water until it became free from acid, and air dried then, oven dried at 50°C and weighed to calculate yield. Microcrystallin cellulose was disintegrated by mortar. Crystallinity of MCC was obtained using a Bruker D8 Advance X-ray diffractometer (Germany). The size of MCC was elucidated by JEOL JEM-1230 transmission electron microscope (TEM) with acceleration voltage of 80 kV. The microscopy probes of the MCC particles were prepared by adding a small drop of the water dispersions onto a Lacey carbon film-coated copper grid then allowing them to dry in air.

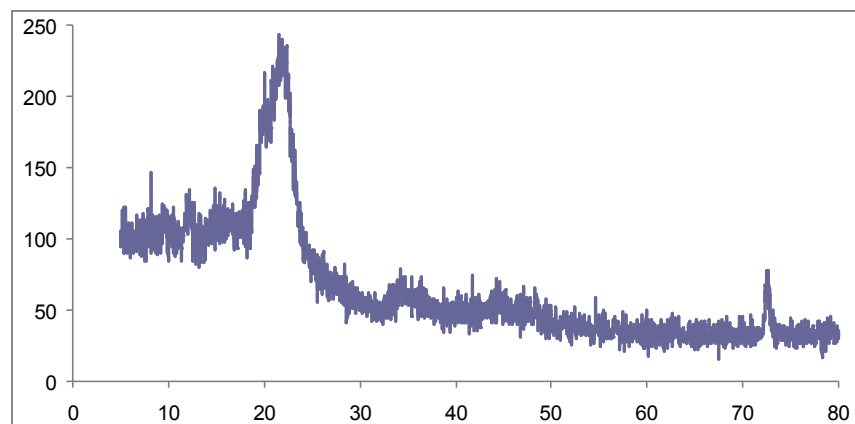
3. Discussion:

3.1 X-ray diffraction (XRD) of microcrystalline cellulose

It is widely recognized that cellulose contains both crystalline and amorphous region (Klemm, Heublein, Fink, & Bohn, 2005) The X-ray diffraction (XRD) patterns of MCC obtained from alpha cellulose of 5% hydrogen peroxide bleached rice straw pulp cooked in this study was illustrated in figure no. 1. The crystallinity of MCC was 45.5 % so the samples had to include cellulose in an amorphous form, which indicates that the cellulose microfibrilles did not become single crystals.

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125 Intensity



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2θ

128 Fig.1 XRD profiles of microcrystalline cellulose

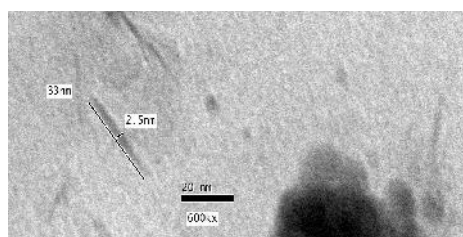
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130 3.2 TEM of MCC

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132 TEM of MCC prepared from alpha- cellulose of H₂O₂ bleached low temperature soda
 133 rice straw pulp was illustrated in figure no. 2. The actual yield of MCC related to alpha
 134 cellulose content of rice straw pulp was 77.32%. MCC having nanoscale was obtained.
 135 The length of this microfibril was 33 nm and its width was 2.5 nm which were in
 136 agreement with other studies (Lepanen & Andersson 2009).

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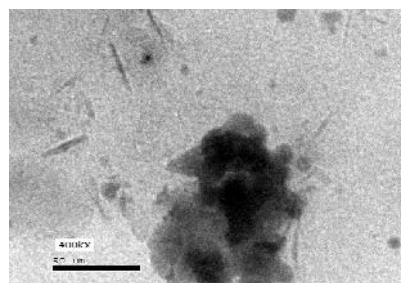


Fig.2: TEM graphs of MCC from alpha- cellulose of bleached (2% hydrogen peroxide) rice straw pulp.

3.3 Structural and strength properties of rice straw pulp

The solid yield of rice straw pretreated with water for 48 hours and pulped using 5% NaOH solution for 2 hour at atmospheric pressure was 74%. Neutral pretreatment is necessary since neutral pH can help to avoid the reactor corrosion problem, which is a major problem of the diluted acid pretreatment process . Also, pretreatment with water improved pulping efficiency of non-wood material and produced pulp containing 68.33% alpha-cellulose. This percent was suitable to prepare microcrystalline cellulose. The oxidative treatment of lignocellulosics by hydrogen peroxide in presence of magnesium sulphate as a stabilizer in an alkaline medium was established. Table 1 indicates effect of H₂O₂ charge on bleached rice straw pulp properties. Pulp obtained using 2% H₂O₂ had 72.727% alpha- cellulose content and 61.5 pulp yield. Yield of bleached pulp using 1 or 4% H₂O₂ was 67.85, 62.9% and had 69.33%, 69.556 alpha- cellulose content respectively at the same conditions. H₂O₂ charge had no effect on burst strength but tensile strength was improved on using 4% H₂O₂ in bleaching. Air permeability of paper sheets made from bleached pulp was greater than the unbleached one. This may be due to increasing the porosity of bleached pulp as a result of losing part of lignin content.

Table 1 physical properties of unbleached and bleached rice straw pulp

pulp	Air permeability, $\text{Cm}^3/\text{cm}^2 \cdot \text{sec.}$	Burst, Kg/cm^2	Tensile strength, Kg
Unbleached pulp	1.275	1.1	2.16
1% H_2O_2 bleached pulp	2.447	1.1	2.23
2% H_2O_2 bleached pulp	2.238	1	2.33
4% H_2O_2 bleached pulp	1.832	1.2	3

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180 3.4 Filler effect on paper properties

181 CaCO_3 is soluble under acid conditions, and therefore requires a near-neutral or slightly
182 alkaline pH papermaking environment (Laufmann, & Hummel, **1991**). To be able to use
183 CaCO_3 as a filler and/or as a coating pigment, numerous paper and board mills around the
184 globe have converted their wet end systems from acid to neutral and slightly alkaline pH.
185 Since calcium carbonate is binder-less and MCC was used as a binder and filler in many
186 studies (Dogan, & McHugh 2007). The effect of these two substances on hand-made
187 paper sheets properties was investigated. Table 2 illustrates this investigation. Binder-less
188 character of CaCO_3 was shown from ash content of unfilled and filled paper sheets.
189 15.1% ash of paper sheets prepared by adding 10% calcium carbonate to beated pulp
190 before sheet making by one hour indicated that it is not a binder to the pulp compared to
191 14.4% ash content of unfilled pulp. 15.1% was reduced to 14.72 and 14.52% at 5%, 2.5%
192 calcium carbonate. Regarding tensile strength of paper sheets, it is improved in presence
193 of all percents of calcium carbonate and MCC prepared in this study in nano scale. MCC
194 forms hydrogen bonds with cellulose, therefore strengthening the fibers. Air permeability
195 is a typical structural property reflecting pores distribution and type and in some way,
196 pores dimension, representing pigment particle packing ability (Santos & Velho 2000)

Air permeability of filled paper was reduced to 0.95% $\text{Cm}^3/\text{Cm}^2.\text{sec.}$ in the presence of MCC filler more than in the presence of calcium carbonate alone 1.32% $\text{Cm}^3/\text{cm}^2.\text{sec.}$ This means that MCC filled paper pores and handicap to air passing through. This is effective on using this paper in packaging and indicates the potential of MCC to be used as a filler to protect food from oxidation reactions. Water permeability of paper sheets was improved in presence of two fillers, it is reduced from 1.4 for unfilled paper to 0.82 litre/sec. on adding 7.5% MCC filler. Paper sheets filled by MCC and calcium carbonate blend have higher water permeability than paper sheets filled with calcium carbonate alone. This is attributed to hydrophilic nature of amorphous cellulose included in MCC. Differences in particle size and particle morphology of the two fillers affect paper sheet properties. Moreover, on several occasions, quite significant discrepancies were found which were attributed to differences in molecular weight, percentage crystallinity and polymorphism(Psomiadou, & Arvanitoyannis 1996; Petersson & Oksman 2006).

Table 2 physical and mechanical properties of unbleached filled pulp

Treated pulp	Air permeability, $\text{Cm}^3/\text{cm}^2.\text{sec.}$	Burst, Kg/cm^2	Tensile strength, Kg	Ash%	Water permeability, litre/ sec.
Unbleached pulp	1.275	1.1	2.16	14.4	1.4
10%calcium carbonate	1.32	1	4.83	15.1	0.62
5%calcium carbonate+5%MCC	0.95	1	4	14.72	0.75
2.5%calcium carbonate+7.5% MCC	0.94	1	3.83	14.52	0.82

3.5 Optical properties of unbleached, bleached and filled pulp

All chemicals used in bleaching rice straw are environmentally friendly substances because they contain hydrogen, oxygen, sodium and magnesium. The bleaching is achieved using a single stage. NaOH is used to bring the pH up to 9 because H_2O_2 becomes active at this pH or oxidation starts at this pH. Table 3 indicates higher

brightness of bleached pulp compared to unbleached one. Adding calcium carbonate alone or mixed with MCC filler to unbleached pulp improves brightness of paper by a small percent, approximately 10.34%. Opacity is a measure of a material's ability to obstruct the passage of light. Sufficient opacity is important to prevent showing printed text or figures on the reverse side of paper sheet. Calcium carbonate and MCC are efficient in terms of opacity for unbleached paper because small internal voids do scatter the light. Enhancement in brightness and opacity of filled paper sheets reflect improved affinity of filler particles to fibers in the aqueous papermaking wet end system. When higher opacity is required, bleaching step can be economically neglected.

Table 3 Optical properties of unbleached, bleached and filled pulp

Sample	Brightness,%	Opacity%
Unbleached control	26.1	77.7
1%H ₂ O ₂ bleached pulp	48.4	96.4
2% H ₂ O ₂ bleached pulp	48.4	97.5
4% H ₂ O ₂ bleached pulp	38.4	97.95
10%calcium carbonate	28.4	99.3
5%calcium carbonate+5%MCC	28.9	99.5
2.5%calcium carbonate+7.5% MCC	28.8	99.1

4. Conclusion:

Rice straw is a locally available waste lignocellulosic non wood material and can be converted into pulp at atmospheric pressure. This pulp can be employed in paper making industry and preparing a valuable product like microcrystalline cellulose. Air permeability, water permeability and mechanical properties of unbleached pulp were improved by adding fillers as calcium carbonate and prepared microcrystalline cellulose. Crystallinity of MCC was 45.5%. Paper sheets filled by MCC and calcium carbonate blend have higher water permeability than paper sheets filled with calcium carbonate alone. . The effect of moisture on packaged products depends on the product. For some,

it is necessary to maintain the moisture content at a high level to prevent the product from drying out. For others the reverse may be the case, as by absorbing moisture the product may loose texture. Burst strength was not affected by fillers. Adding calcium carbonate alone or mixed with MCC filler to unbleached pulp improves brightness of paper by a small percent approximately; 10.34%. Calcium carbonate and MCC are efficient in terms of opacity for unbleached paper because small internal voids do scatter light. Enhancement in brightness and opacity of filled paper sheets reflect improved affinity of filler particles to fibers in the aqueous papermaking wet end system. When higher opacity is required, bleaching step can be economically neglected.

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