



Trade Science Inc.

Environmental Science

An Indian Journal

Current Research Papers

ESAIJ, 4(6), 2009 [530-536]

Egyptian rice straw application for useful products throughout chemical treatments

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Received: 10th October, 2009 ; Accepted: 20th October, 2009

ABSTRACT

Egyptian rice straw was collected from El-Delta region and subjected to new method of treatment in order to transfer it to cellulose pulp which would be a primary substance for many useful products. The new method was mechanical pulping with soda process conditions, the product of this treatment was obtained and characterized with both chemical and instrumental analysis namely IR analysis depending upon some methods for both qualitative and quantitative purposes.

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KEYWORDS

Egyptian rice straw;
Mechanical pulping;
Soda process;
IR analysis.

INTRODUCTION

Rice straw still a waste till now all over the world and especially in Egypt, since there is no way to turn it to useful products on the wide range. So, this paper will discuss the use of rice straw for the production of cellulose^[1].

There are many methods known for the extraction of cellulose from its sources generally and rice straw especially, these methods could be classified into main three categories depending on the condition of treatment, mechanical treatment, semi-chemical, and chemical treatment methods^[2].

Soda extraction method for mechanically devided rice straw (semi-chemical) was used in this study. IR analysis is undertaken to describe the produced cellulose^[3,4].

Saad, et al.^[4], in an article on the silylation of cellulose gave a collective assignment for the infrared ab-

sorption spectra of the different kinds of cellulose and tabulated the main important bands of each kind. Their TABLE is actually very beneficial for obtaining the assignment of IR bands of cellulose materials. Hence, this TABLE is considered to be of great help for assigning the IR spectra of rice straw pulps obtained under different conditions of cooking of rice straw with sodium hydroxide solutions (pulping).

For the determination of lignin content, Issa and Saad *et al.*^[3,5] developed a method for the use of IR spectrum to determine the lignin content in cellulose samples from different sources. The relative intensity values (I_{rel}) were calculated from the relative absorbance values (A_{1606}/A_{898}) using the background correction method. The base line was taken between 1606 and 898 cm^{-1} bands.

Accordingly, the lignin content could be determined in the above mentioned range using the following linear equation:

$$\text{Lignin \%} = 9.27 + 3.12 \times I_{re} \tag{1}$$

Also, the lignin content was found to be directly proportional to the intensity of the bands at 1510 and 1740 cm⁻¹. Karklin and Gromov^[6] developed a method for the rapid determination of lignin content (x) in sulphate pulp using the intensity of the band at 1595 cm⁻¹ relative to that at 893 cm⁻¹ (M). The following equations were given:

$$X = 34.2 M - 19.3 \tag{2}$$

(where M=0.93-0.56), and

$$X = 10.3 M + 3.0 \tag{3}$$

(where M=1.90-0.93).

The above mentioned principle was also used by Karklin and Kreicberga^[7] to determine the lignin content in wood. The base line was constructed by connecting the absorption at 1850 cm⁻¹ and 800 cm⁻¹. The lignin content was determined from the relations:

$$X = 12.01 M + 6.23 \tag{4}$$

(for M=1.3-3.53), and

$$X = 4.24 M + 33.9 \tag{5}$$

(for M=3.53-16).

Karklin and Kreicberga^[7] determined the lignin content in nitric acid pulp from birch wood by measuring the relative optical density of the infrared absorption band at 1595 cm⁻¹, calculated from an internal standard at 895 cm⁻¹ and an external standard K₄Fe(CN)₆ at 2110 cm⁻¹, and plotting a calibration curve. Marton and Spark^[8] showed that the lignin content can be determined by infrared multiple internal reflectance. The intensity of the 1510 cm⁻¹ lignin band relative to that of the cellulose band at 1310 or 893 cm⁻¹ is proportional to the lignin content.

- (a) In Saad *et al.*^[4] method: the relative intensity values (I_{rel}) were calculated from the relative absorbance values (A₁₆₀₆/A₈₉₈) using the background correction method. The base line was taken between 1606 and 898 cm⁻¹ bands.
- (b) In background correction method^[9], the base line was taken between 1850 and 850 cm⁻¹.
- (c) In the base line technique method^[10], two lines

were constructed between the three points representing the minimum absorbance values within the 2000 to 650 cm⁻¹ range, namely between 1850 and 1550 cm⁻¹ as well as 1550 and 850 cm⁻¹.

- (d) In the Pisolot method^[11], the base line is constructed below the absorption band considered. The two base lines were obtained by connecting the absorbance at 1550 and 1780 cm⁻¹ as well as at 870 and 930 cm⁻¹ for the two bands respectively.

EXPERIMENTAL

Analysis of raw materials

Many methods for the analysis of plant materials and pulp have been developed and tested for their reliability. The standard methods mostly in current usage nowadays are the American Tappi Standard, the German (Deutsche Einheiten) methods, and the Swedish methods^[12].

In this work the Tappi standards were used in most of the chemical analysis of the raw material and pulp.

Moisture content of both rice straw samples and the prepared cellulose were determined. Also, combustible organic matters and water soluble matters were determined. The composition of the rice straw and cellulose samples were confirmed by elemental analysis, IR spectra. The thermal studies were carried out using TGA-50 and DTA-50, Shimadzu Thermogravimetric analyzer (Japan), with the rate of heating 10°C/min. SEM were employed.

RESULTS AND DISCUSSION

Analysis of raw materials

TABLE 1 : The approximate composition of dry rice straw

Sample number	I	II	III
Moisture	10 %	10 %	12 %
Water soluble matters	10 %	12 %	10 %
Fibrous part	65 %	66 %	62 %
Ash	15 %	12 %	16 %

TABLE 2 : Pulping of rice straw

Factor	sodium hydroxide concentration				Time of pulping				weight/volume ratio (w/v)				Temperature of pulping degree cent.			
	6%	8%	10%	12%	1hr	2hrs	3hrs	4hrs	1/5	1/10	1/20	1/50	40	60	80	100
Condition	65	58	47	47	60	47	44	44	51	49	47	47	75	70	60	47
Yield																

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Cooking conditions

Effect of the nature of rice straw on the pulp yield

The effect of rice straw nature (plant shape and length) was studied by subjecting the plant as a whole (varies from 80-120 cm length) and securing it into small sizes manually (20, 10 and 5 cm) comparing with the plant divided by mechanical ways, for cooking with sodium hydroxide solution (10%) for two hours when boiling. The results of these experiments are reported in TABLE 3.

TABLE 3 : The effect of rice straw nature on the pulp yield

Sample length	The hole plant	20 cm	10 cm	5 cm	Mechanical divided plant
Wt0 g.	10	10	10	10	10
wtf g.	6.11	5.19	5.27	4.9	4.66
Loss	3.89	4.81	4.73	5.1	5.34
Yield %	61.1	51.9	52.7	49	46.6

The industrial conditions of pulping rice straw usually operates in batch reactors with a temperature between 160 and 180 °C and a cooking time between 4 and 6 hours. The raw material is treated with a highly alkaline solution of NaOH (12-15%) concentration.

From the results obtained in TABLES 2 and 3, cooking conditions could be reduced to 10% sodium hydroxide solution for 2 hours boiling when it is mechanically divided (semi-chemical pulping). This reduction did not affect the yield of the produced pulp so much, these conditions would give yield of about 47% with cellulose not less than 90%.

Alpha cellulose estimation

The term α -cellulose allows us to describe the quality of the raw materials and its competitiveness in the field of rice straw usage especially for paper production. From the results we observe that rice straw is low in α -cellulose content (28%) but it still has its importance in this field. Cooking with sodium hydroxide affects the α -cellulose content of rice straw. It rises it till about 90% when boiling with (10%) sodium hydroxide concentration for 2 hours.

TABLE 4 : α -cellulose content of rice straw and pulp from rice straw

Sample no.	I	II	III	IV	V	VI
α -cellulose %	28	29	28	65	75	90

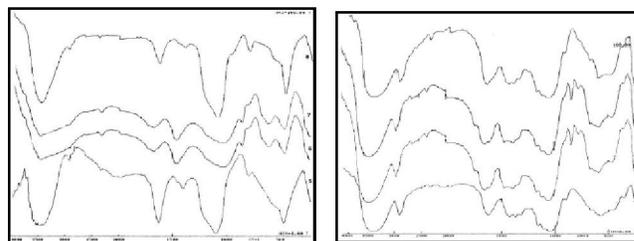


Figure 1 : IR absorption spectra of samples 1, 2, 3, 4, 5, 6, 7 and 8

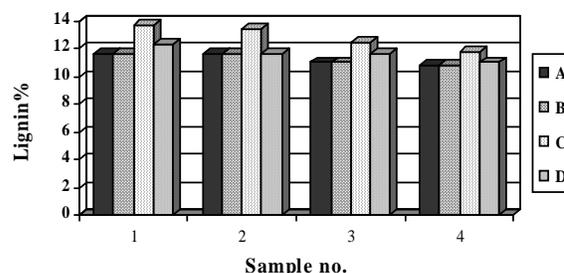


Figure 2 : The relation between sodium hydroxide solution concentration and the lignin content determined by different methods from IR charts when pulping for 1 hours

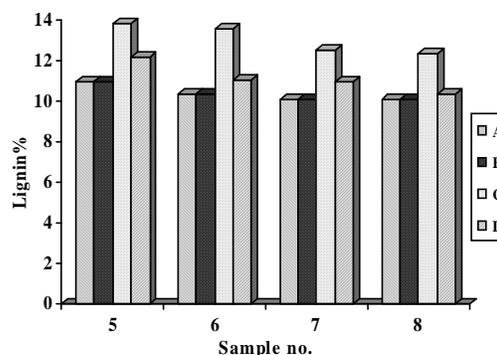


Figure 3 : The relation between sodium hydroxide solution concentration and the lignin content determined by different methods from IR charts when pulping for 2 hrs where:

- A) The lignin content determined using Saad et. al. method.
- B) The lignin content determined using the background correction method.
- C) The lignin content determined using the base line technique method.
- D) The lignin content determined using the pistol method^[11].

TABLE 5 : The relation between sodium hydroxide solution concentration and the lignin content determined by different methods from IR charts

Sample no.	1				2			
	Time							
NaOH conc.	1 hr.				2 hrs.			
	4 %	6 %	8 %	10 %	4 %	6 %	8 %	10 %
A	11.61	11.59	11.02	10.83	10.96	10.33	10.12	10.10
B	11.61	11.59	11.02	10.83	10.96	10.33	10.12	10.10
C	13.67	13.45	12.51	11.79	13.85	13.58	12.48	12.38
D	12.36	11.61	11.6	11.02	12.14	11.05	10.95	10.33

Infrared spectrophotometric study of cellulose from high yield soda rice straw pulps**TGA studies of cellulose samples**

The IR spectra of cellulose materials were the subject of many studies^[13]. Isaa, Saad and Fahmy^[4], in an article on the silylation of cellulose gave a collective assignment for the infrared absorption spectra of the different kinds of cellulose and tabulated the main important bands of each kind. The band assignments given by previous authors in many studies were helpful in obtaining the correct assignment for the various bands in the IR spectra of rice straw pulp samples obtained under different cooking conditions^[9]. On comparing the spectrum of the raw material with those of high yield soda rice straw pulp the following can be pointed out:

a- The broad δOH band at 1600 cm^{-1} tends to be less broad in the spectra of the pulps, meanwhile the band envelopes become more symmetrical. The bands due to the stretching vibrations of the CH-groups tend to be sharper in the spectra of the pulps with the loss of absorption on the higher frequency side where the bands due to aromatic CH-groups appear. The group of bands within the $1400\text{-}1200\text{ cm}^{-1}$ becomes sharper with rise of either NaOH concentration or cooking temperature. The intensity of most bands decreases in the same direction while the peaks at $1630\text{-}1370\text{ cm}^{-1}$ tend to be sharp and display a slight increase in peak intensity. The bands within the $1200\text{-}900\text{ cm}^{-1}$ region tend to be less broad in the spectra of the pulps, yet the most obvious change in this region is the appearance of some sharp peaks near 1100 cm^{-1} . These changes recall more or less those observed with mercerization of cellulose and can be similarly accounted for^[14]. The absorption bands within the $800\text{-}625\text{ cm}^{-1}$ region show some intensity changes on cooking rice straw with NaOH. These spectral changes can be due to dissolution of lignin and as well as the removal of some low molecular forms of carbohydrates from rice straw during the pulping process. This is accompanied by the large decrease in the intensity of the absorption bands due to such components in the various regions; hence the other absorption bands appear sharper. The sharpness of these bands is more obvious with samples cooked for longer times or when the NaOH concentration was increased. Also the rise of cooking temperature brings almost similar effects.

b- The strong band at 1735 cm^{-1} , assigned to the stretching vibration of the C=O group of the acetyl residue from polyurinoide of the hemicelluloses, displays an obvious decrease in intensity when rice straw is cooked in 6 % NaOH for one hour at $100\text{ }^{\circ}\text{C}$ on increasing the time of cooking to two hours, the band is turned to a very shallow broad one but it vanishes completely when the rice straw is cooked with 8 % NaOH for 2 hrs. at boiling. The band appears as a rudimentary peak in the spectrum of samples cooked for one hour at boiling temperature with 8 % NaOH. Also this absorption peak is not observed in the spectra of samples cooked with 10 % NaOH. The decrease of C=O band intensity and its vanishing in the spectra of the pulps is due to the hydrolytic rupture of the acetyl linkage between lignin and hemicellulose during the pulping of rice straw with NaOH. The removal of the acetyl group from rice straw increases with cooking time or rise of NaOH concentration and also by increasing the temperature of the cooking.

c- The bands at $1595\text{-}1600\text{ cm}^{-1}$, which correspond to the skeletal vibrations of the aromatic rings of the lignin part, show a gradual decrease on increasing the cooking time or with rise of temperature and or alkali concentration. The drop in the intensity of this band denotes that the lignin content of the pulps decreased during cooking with various degrees depending on the prevailing experimental conditions.

The whole rice straw starts to degrade thermally at about $250\text{ }^{\circ}\text{C}$. But in the temperature range $300\text{-}375\text{ }^{\circ}\text{C}$, the majority of the carbohydrate polymers have degraded and only lignin remains. The hemicellulose components start to decompose at about $225\text{ }^{\circ}\text{C}$ and are almost completely degraded by $325\text{ }^{\circ}\text{C}$. The cellulose polymer is more stable to thermal degradation until about $370\text{ }^{\circ}\text{C}$, and then decomposes almost completely over a very short temperature range. The lignin starts to decompose at about $200\text{ }^{\circ}\text{C}$, but is much more stable to thermal degradation as compared to the carbohydrate polymers^[15].

Figure 4 and TABLE 6 show that there are three different thermal loss stages. The first stage representing a weight loss of 11.801, 14.979, 6.123 and 7.505% which may be attributed to the loss of moisture content from samples 3, 7, 8 and 10 respectively. The second

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stage at 300–325 °C is suggested to be due to the thermal degradative oxidation of the carbon content, its ratio reached 30.35, 35.582, 57.790 and 57.731% of the total weight for 3, 7, 8 and 10 respectively. The third stage at 470–1000 °C involves weight loss of 25.619, 21.785, 22.891 and 28.24% which may be due to the complete oxidation of the remaining organic matter.

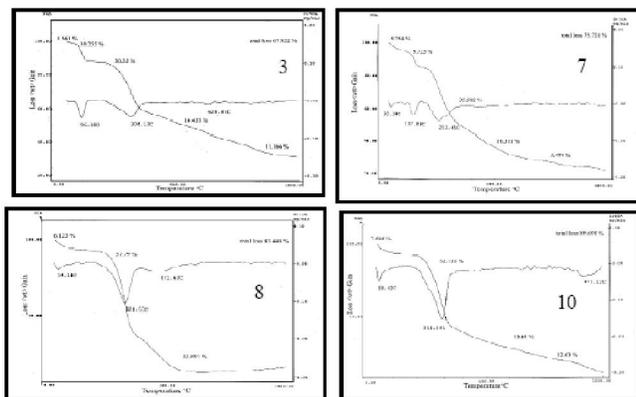


Figure 4 : TGA thermograph of samples 3, 7, 8 and 10

TABLE 6 : TGA analysis for cellulose samples

Temperature range	Weight loss			
	Sample 3	Sample 3	Sample 3	Sample 3
35-100°C	11.801	14.979	6.123	7.505
300-325°C	30.35	35.582	57.790	52.731
470-1000°C	25.619	21.785	22.891	28.24
Total weight loss	67.952	75.72	83.44	89.698
Remained ash	32.048	24.28	16.56	10.302

The positions of weight loss on the TGA traces are shifted to higher temperatures, for increased processing stages from pre-washed to chemically treated rice straw indicating increased thermal stability. This increase of thermal stability could be due to the decreased lignin and hemicellulose content.

Differential thermal analysis (DTA) of cellulose

In Figure 5 there is an endothermic peak at 90 °C which is due to moisture content loss, and there are two exothermic peaks at 350 and 470 °C which are assigned to oxidative degradation reaction. Also, both TGA and DTA analyses confirmed each other. Thus, rice straw and rice straw pulp samples composition are about 10% moisture, 15% ash and 75% organic portion which are oxidized at two steps with the portion 45 at the first one and 25 at the second step.

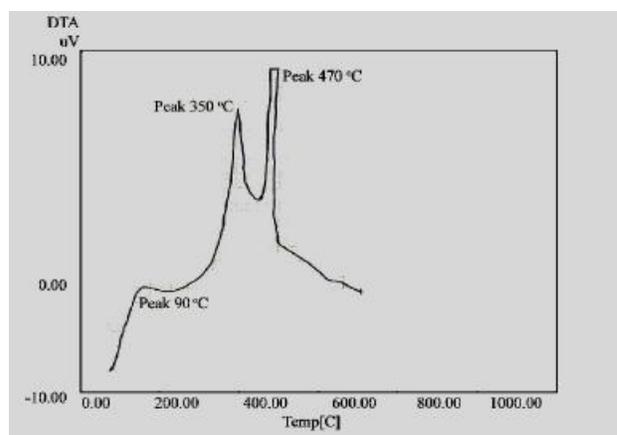


Figure 5 : DTA thermograph of rice straw pulp sample no. 8

Kappa number (permanganate number) determination

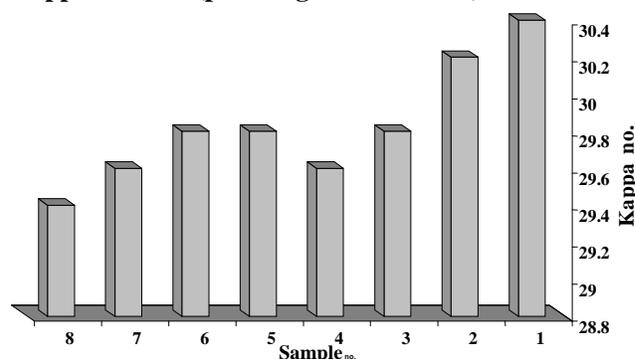


Figure 6 : Kappa number for samples 1, 2, 3, 4, 5, 6, 7 and 8

TABLE 7 : Kappa no. of pulp from rice straw according to relative intensity

Sample no.	1	2	3	4	5	6	7	8
Kappa no.	30.4	30.2	29.8	29.6	29.8	29.8	29.6	29.4

Figure 6 shows the relationship between the extents of delignification (Kappa number is the volume in milliliters of 0.1N potassium permanganate solution consumed by one gram of moisture-free pulp) under the conditions specified in this method. It is found that delignification of rice straw can be done successfully in all cases of cooking conditions.

SEM investigation^[16]

SEM is a powerful and effortless technique to image the fibers in micrometer scale. The physical trends like the removal of fines and fillers, or the different nature of hardwood and softwood fibers can be visualized with SEM. In fact, SEM measurements had the strongest link to the bulk properties of the pulp samples. From the results of this part we can conclude that rice straw can have qualities compared with virgin fibers

when processed correctly^[17].

The super molecular structure of the blank (mechanically divided rice straw) and that treated with sodium hydroxide samples were studied by electron microscopy Figure 7.

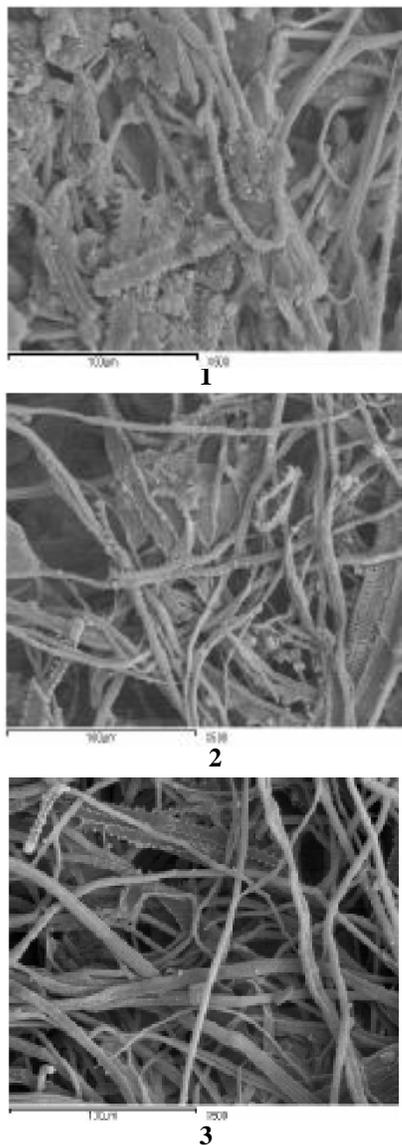


Figure 7 : SEM of rice straw pulp samples nos. 1, 5 and 8

When the samples were treated with different concentration of alkali, the fibers tended to agglomerate gradually into small and large bundles.

Alkali treated samples with 4% and 10% alkali concentrations respectively showed that many bundles aggregation showed the decrease of voids between them which confirmed the increase in the degree of polymerization and crystallinity.

Increasing the alkali concentration, the degradation

products were more pronounced with large spaces between them as in case of alkali treated pulp with 10% (Figure 7). The appearance of dots are most likely tiny degraded products which have been formed on the fracture surface of the cellulose pulp.

Samples key

- | | |
|---|--|
| 0 | Rice straw sample |
| 1 | Rice straw sample treated with sodium hydroxide solution (6 %) for 1 hr. |
| 2 | Rice straw sample treated with sodium hydroxide solution (8 %) for 1 hr. |
| 3 | Rice straw sample treated with sodium hydroxide solution (10 %) for 1 hr. |
| 4 | Rice straw sample treated with sodium hydroxide solution (12 %) for 1 hrs. |
| 5 | Rice straw sample treated with sodium hydroxide solution (6 %) for 2 hrs. |
| 6 | Rice straw sample treated with sodium hydroxide solution (8 %) for 2 hrs. |
| 7 | Rice straw sample treated with sodium hydroxide solution (10 %) for 2 hrs. |
| 8 | Rice straw sample treated with sodium hydroxide solution (12 %) for 2 hrs. |

CONCLUSION

At first, from the analyses above we could conclude that rice straw is one of the most rich sources for cellulose production and with very easy method we could transfer it into cellulose pulp with appreciable degree of purity for many industrial purposes.

Secondly, mixing between chemical and mechanical treatment for transferring agricultural waste in general and rice straw especially is a good method as it reduces both the time of treatment and the amount of chemicals used and hence the produced black liquor as the waste of that industry.

Thirdly, by using the IR analysis, TGA, DTA analyses and SEM for both qualitative and quantitative analyses for rice straw and the produced cellulose from the four proposals already mentioned above is a useful manner.

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