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Rice straw as a new resource for some beneficial uses

F.A. Abdel-Mohdy [a], E.S. Abdel-Halim [a], Y.M. Abu-Ayana [b,*], S.M. El-Sawy [b]

[a] Textile Research Division, National Research Centre, Dokki, Cairo, Egypt
[b] Department of Polymers and Pigments, National Research Centre, Dokki, Cairo, Egypt

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ABSTRACT

The objective of the present work is to make an environmental impact assessment study for the production of beneficial materials from rice straw. Rice straw has been liquefied, and a number of liquefaction variables have been investigated to determine the optimal liquefaction conditions. Results show that the reaction conditions, such as catalyst concentration, liquefaction temperature, time and material to liquor ratio are of great influence on the liquefaction process. Liquefaction of rice straw was carried out directly after grinding and also after pulping process. Preparation and evaluation of carboxymethyl cellulose from cellulosic materials obtained from rice straw was carried out. The work was extended to the extremely fine white grayish powder that was obtained on burning rice straw and/or the residues obtained after liquefaction process of rice straw at 550 °C. The remaining powder was characterized and evaluated; X-ray analysis showed that about 69% of this remainder was found as silica. The size of the particles ranged from 18 to 68 nm. The powder was tested for application as a filler or extender pigment in some paint formulations, promising results were obtained.

1. Introduction

From the data available, the quantity of rice straw produced per year in the world was probably about 570 million tones (Van Nguu Nguyen, 2000). Rice straw is the residue and the excesses of production of rice that was not utilized. Although such residues contain materials that can benefit society, their apparent value is less than the cost of collection, transportation and processing for beneficial use. As a result, the waste discharged can cause environmental problems and a loss of natural resources. If the wastes can be utilized, such as to enhance food production, they are no longer wastes but become new resources.

With an increase in crop yields and cropping intensity, the management of rice by-products is becoming a problem as well as an opportunity. In traditional rice cropping systems, rice straw was either removed from the field at harvest time and stored as stock feed, or burnt in the field. While straw burning is still practiced in many countries, it is increasingly becoming unacceptable because of environmental and health concerns.

At harvest, the moisture content of straw is usually more than 60% on a wet basis, however, in dry weather straw can quickly dry down to its equilibrium moisture content of around 10–12%. Rice straw has a high ash content (up to 22%) and low protein content. The main carbohydrate components of rice straw are hemicellulose, cellulose and lignin. High silica content in rice straw (9–14%), however, prohibits the economic use.

It is clear from the collected data that the most traditional uses of rice by-products includes straw and hull for energy, animal feed, building materials and paper production (Van Nguu Nguyen, 2000).

Cellulose is a linear polymer of β-anhydroglucose units. Each anhydroglucose unit contains three hydroxyl groups. Carboxymethyl cellulose (CMC) is prepared by the reaction of the cellulose hydroxyls with sodium monochloroacetate as follows: (Davidson, 1980) $\mathrm{Cell{-}OH + NaOH + ClCH_2COONa \rightarrow Cell{-}O{-}CH_2COONa + NaCl + H_2O}$.

The extent of the reaction of cellulose hydroxyls to form a derivative is called the degree of substitution (DS) and is defined as the average number of the three hydroxyl groups in the anhydroglucose unit which have reacted. Thus, if only one of the three hydroxyl groups has been carboxymethylated, the DS is 1.0. Commercial products have DS values ranging from 0.4 to about 1.4. The most common grade has a DS of 0.7–0.8.

This research work is directed towards the use of chemical methods for conversion of rice straw to valuable industrial products. The main purpose of this work is to achieve: (a) preparation and evaluation of carboxymethyl cellulose (CMC), (b) preparation, characterization and evaluation of the silica powder obtained from rice straw and rice straw residues.

2. Experimental

2.1. Materials

Rice straw was supplied as agriculture wastes from the field at harvest time. The dried straw was ground, and used without further purification.

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* Corresponding author.
E-mail address: yosreya20@gmail.com (Y.M. Abu-Ayana).

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Filler and extender pigments, resins, solvents and all chemicals used are products of different local and international companies.

2.2. Liquefaction of rice straw

The liquefaction experiments were carried out in a small stainless steel reactor. The reactor was charged with the solvent (dioxane–water), catalyst (sulphuric acid), and rice straw. The reactor was closed tightly and heated to specified temperature for specified time. At the end of time, the reactor was cooled down to quench the reaction (Abou-Yousef, El-Sakhawy, El-Barbary, & Kamel, 2003). The resulting mixture was filtered to separate any residue (insoluble part) from the solution. The insoluble residue was washed, dried overnight in a convention oven at 105 °C, and weighed to determine the residue content.

The solvent was removed from the filtrate using Rota vapor evaporation. The remainder solution was poured on excess methanol, cellulose was precipitated and separated by filtration and washed several times with methanol, dried in a convention oven, while lignin and other undesired materials removed in filtrate.

2.3. Delignification/pulping

Delignification was carried out during pulping and liquefaction processes. The objective of this process is to investigate the production of high-yield pulp and good strength properties (Hebeish, 1987).

Rice straw was added to NaOH solution (20 g/l) in a material to liquor ratio of 1:10. The mixture was heated in an autoclave at temperature of 130 °C for a minimum 2 h. The pulp was extracted and washed with cold tap water to complete purity. Bleaching was then carried out with hypochlorite solution (1.5 g/l) in a single stage bleaching process at room temperature for 1 h.

2.4. Carboxymethylation

Carboxymethyl cellulose (CMC) was prepared from rice straw after liquefaction or pulping processes through one of the following techniques.

2.4.1. First process

A CMC sample was prepared by the nonaqueous method (Hebeish, 1987; Hebeish, El-Sisi, Ragheb, Kashouti, & Badr El-Din, 2002). 100 g of pulped rice straw were added to a mixture of 630 ml of ethyl alcohol and 554 ml of toluene, followed by addition of 50 ml of 50% aqueous sodium hydroxide under stirring for 30 min at 30 °C. A calculated amount of monochloroacetic acid (80 g/100 g pulped rice straw) was then added gradually. The temperature was raised to 70 °C and maintained at this degree for 3 h. The reaction mixture was left overnight; the excess of caustic soda was neutralized with glacial acetic acid, and the product was filtered and purified by washing with aqueous ethanol under stirring. The process may be repeated up to the degree of purity required.

2.4.2. Second process

Carboxymethylation was carried out by a slurry method (Dapia, Santos, & Parajo, 2003). Pulped rice straw (3 g) was dispersed in isopropyl alcohol (180 ml) and kept under mechanical stirring for 30 min at room temperature. Eight milliliter of 50% NaOH (w/v) was added drop wise in about 10 min and the mixture was left under stirring for 60 min at room temperature. Seven gram of monochloroacetic acid was dissolved in 15 ml of isopropyl alcohol and added to the mixture portion wise. The temperature was raised to 60 °C and the mixture was allowed to react under stirring for 60 min. The mixture was then filtered, suspended in 150 ml of 80% methanol and neutralized with acetic acid. The final product was washed three times with 70% methanol and dried at 60 °C.

2.4.3. Third process

In this process, cellulosic product which was obtained from liquefaction of rice straw was used for preparation of CMC by the same technique as in the second process.

2.5. Burning process

Insoluble part (residue) obtained from liquefaction process of rice straw, cellulosic product obtained from pulping process of rice straw and rice straw supplied from the field at harvest time, were burnt in muffle furnace to identify the inorganic matter included in the samples.

A silica crucible was cleaned and ignited to constant weight in a muffle furnace. The weighed sample was placed in the crucible and burnt on the hearth of the furnace till it was well carbonized, then the temperature was raised to 550 °C, and heating continued to burn off all carbon. After complete ignition, the covered crucible was placed in a desiccator and allowed to cool to room temperature.

2.6. Analysis

2.6.1. Degree of substitution (DS) of prepared CMC

The water soluble sodium carboxymethyl cellulose is converted to the insoluble acid form, purified by washing, dried and then a weighed sample is reconverted to the sodium salt with a measured excess of sodium hydroxide.

The carboxyl content was determined by the alkalimetery method (Daul, Reinhardt, & Reid, 1953). The degree of substitution (DS) was calculated from% carboxyl as follows:

$$\text{number of carboxymethyl group in1 g CMC } (X) = \frac{\mathrm{N_1V_1{-}N_2V_2}}{1000 \times \mathrm{W}}$$

$$\text{and DS} = \frac{162 \times \mathrm{X}}{1 - 58\mathrm{X}}$$

where

N_1 = normality of NaOH solution (which is equal to molarity M in this case).
V_1 = milliliters of NaOH solution added
N_2 = normality of HCl (which equals molarity)
V_2 = milliliters of HCl required for titration of the excess NaOH
W = weight of CMC used
162 = molecular weight of the anhydroglucose unit of cellulose.
58 = net increase in molecular weight of anhydroglucose unit for each carboxymethyl group substituted.

2.6.2. Solubility of CMC

Water solubility of prepared CMC was determined according to method of Kunin (1958), by repeated soxhlet extracting using water (for 2 h, two times).

$$\%\text{loss in weight} = \frac{w - w^{-}}{w} \times 100$$

where: w and w^{-} are weight of sample before and after extracting in gram, respectively.

2.6.3. IR spectrometry

IR spectra were recorded on a Jasco FT/IR 300 E Fourier Transform Infrared Spectrometer. IR was performed at National Research Centre, Egypt.

2.6.4. X-ray analysis

X-ray analysis of the powder remained after burning rice straw was carried out by X-ray diffractometer (Daino-8000, Co K_α radiation). The X-ray was energized by 45 K.V. and 10 mA. Step-Scan mode with step 0.1° 2Θ and time of step 1 s 2Θ range from 20° to 80°.

X-ray fluorescence of the remained powder was carried out using AXIOS, Wavelength Dispersive-XRF Sequential Spectrometer (PANalytical 2005).

2.6.5. Particle shape

The particle shape of the powder sample remained after burning rice straw was examined using transmission electron microscope (EM Zeiss, West Germany).

2.7. Characterization and evaluation of the remained powder

The powder remained after burning rice straw and rice straw residues was characterized and evaluated as an extender pigment according to well known and standard methods. Solubility: ASTM D 1208-52 T. Hydrogen ion concentration (pH value): ASTM D 1208-28-1975. Specific gravity: ASTM D 153-54. Bulking value: ASTM D 16-62. Oil absorption: International Organization for Standardization Technical Committee ISO/TC 35. Bleed test and chemical resistance (Payne, 1961).

2.8. Paint preparation and application

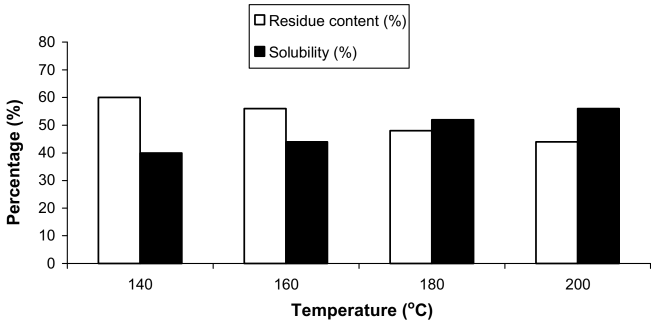
The obtained powder under investigation was tested as an extender pigment; it was incorporated in some paint formulations. The formulated paints were prepared by dissolving the binder mixture in suitable solvents. The pigment mixture was then ball milled with some of the vehicle solution for three hours. The remainder of the vehicle was then added to get the ready mixed paints. The paints were carefully screened before application, during which the ingredients were kept properly mixed.

Film applicator was used for application of paints on the panels so as to obtain smooth and uniform films. Wet painted panels were kept protected against damage from dust or other foreign matters as much as practically possible.

2.8.1. Methods of testing and evaluation of the paint films

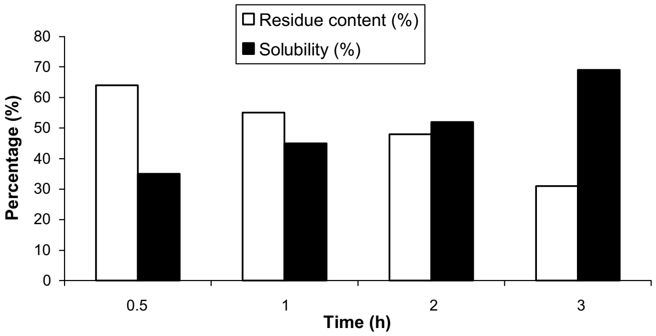
The formulated paints were tested and evaluated according to well known standard methods:

a) Preparation of glass panels: ASTM D3891–80.
b) Preparation of tin panels: ISO 1614:1993 (E).
c) Dry film thickness on glass plates using Erichsen thickness gauge.



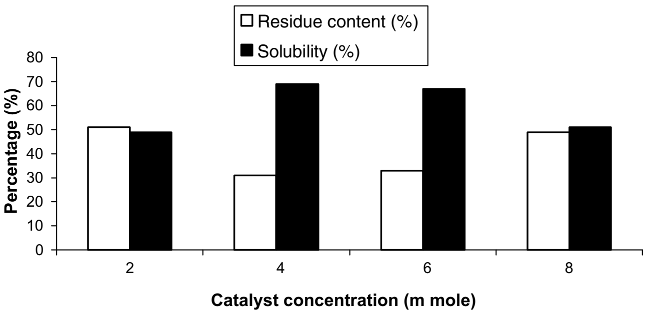
2.5 g RS; M/L ratio, 1:30; dioxane / water, 3:1; [catalyst], 4 m mole; 2h

Fig. 1. Effect of temperature on residue content and solubility yield.



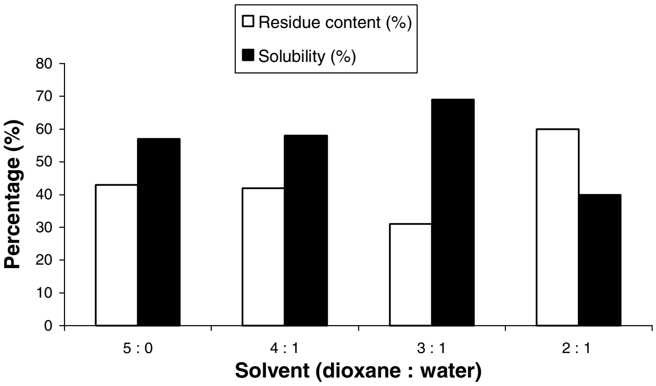
2.5 g RS; M/L ratio, 1:30; dioxane / water, 3:1; [catalyst], 4 m mole; 180 °C

Fig. 2. Effect of time on residue content and solubility yield.



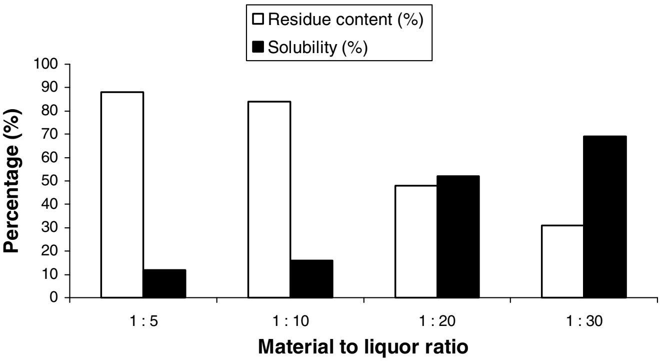
2.5 g RS; M/L ratio, 1:30; dioxane / water, 3:1; 180 °C; 3 h

Fig. 3. Effect of sulphuric acid catalyst on residue content and solubility yield.



2.5 g RS; M/L ratio, 1:30; [catalyst], 4 m mole; 180 °C; 3 h

Fig. 4. Effect of solvent composition on residue content and solubility yield.



2.5 g RS; dioxane / water, 3:1; [catalyst], 4 m mole; 180 °C; 3 h

Fig. 5. Effect of material to liquor ratio on residue content and solubility yield.

d) Hardness of the paint films (measured at 30 μm): using the hardness tester DIN 53 157.
e) Adhesion test: ASTM 3359–74 part 27 (1975).
f) Ductility: was measured by the cupping test machine DIN 50 101.
g) Acid resistance test: a solution of 20% HCl was used ASTM D 287–74.
h) Alkali resistance test: a solution of 5% NaOH was used ASTM D 1647–70.

Table 1
Delignification of rice straw during methods of processing

Delignification process	Liquefaction content%		
	Residues content	Dissolved content	Noncellulosic compounds and lignin
Liquefaction process	25	75 (cellulose)	25
Pulping process	50	50	50

3. Results and discussion

3.1. Liquefaction of rice straw

Figs. 1–5 show the dependence of the residue content and accordingly the solubility on the liquefaction variables such as temperature, time, catalyst concentration, solvent composition and material to liquor ratio.

Results in Fig. 1 show that the residue content decreased with increasing the liquefaction temperature from 140 to 200 °C. Accordingly, it was concluded that higher temperatures accelerate the liquefaction process.

In Fig. 2, it is clear that the solubility increased with increasing the time of liquefaction, i.e, the residue content (%) decreased with increasing time.

Results in Fig. 3 revealed that the residue content (%) significantly decreased with increasing catalyst concentration from 2 to 4 mmol. It is clear that the minimum acid concentration that gave a high liquefaction yield was (4 mmol), i.e., it was the optimum catalyst concentration to study the other factors.

The effect of solvent composition on the liquefaction process was studied. Fig. 4 indicates that, using 3:1 dioxane:water solution

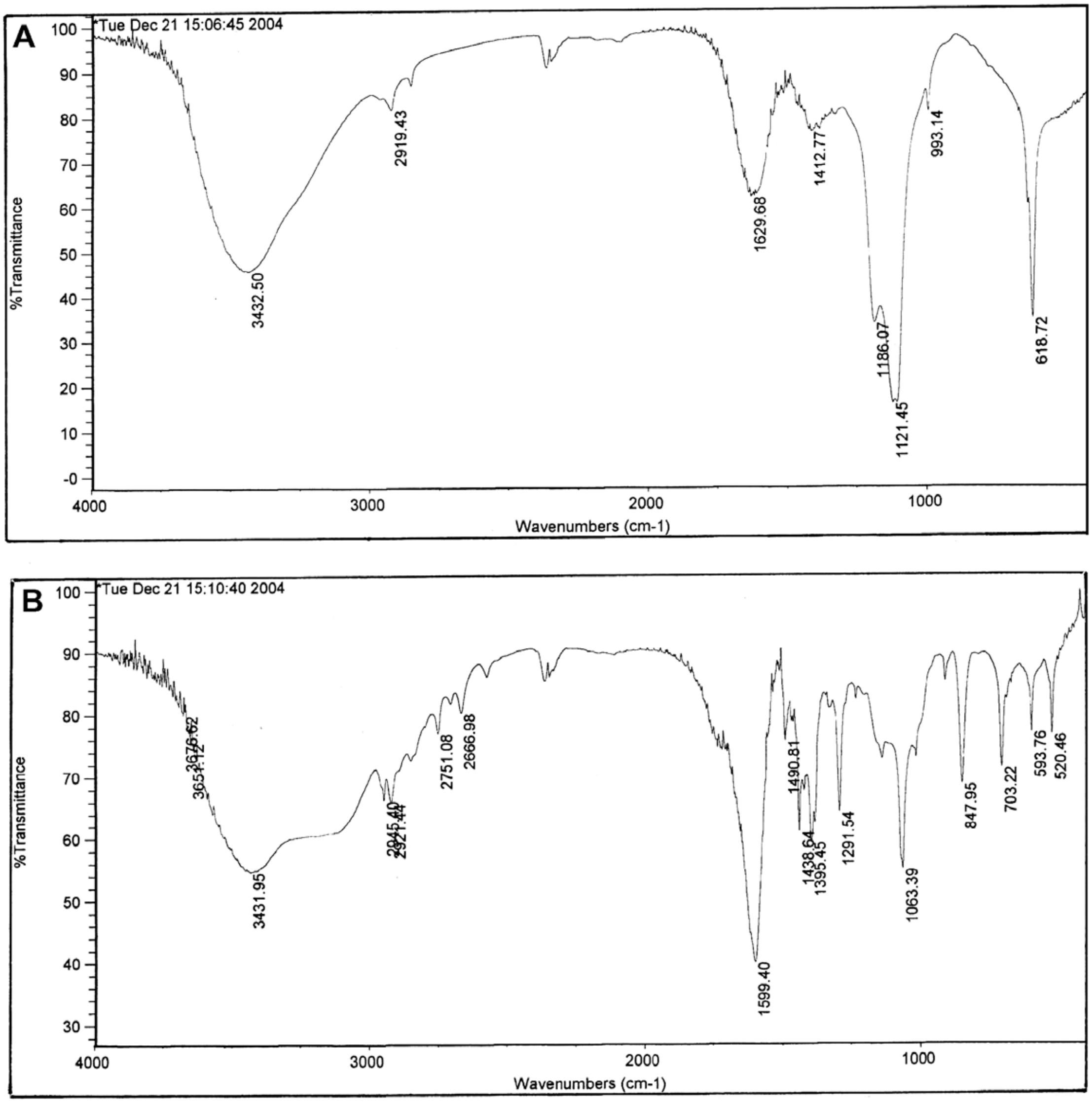


Fig. 6. Infrared spectra of carboxymethyl cellulose (CMC): (A) prepared CMC, (B) commercial CMC.

Table 2
Physical and chemical properties of CMC prepared by different processes

Preparation processes	Solubility%	COOH content (mmol/100 g)	DS
First process	50	215	0.398
Second process	90	230	0.429
Third process	100	230	0.420

gives the optimum reduction in the residue content (%), this may be due to the hydrolysis effect. However, further replacement of dioxane with water increased the residue content. Also it was found that the 30:1 material to liquor ratio gave the highest liquefaction yield as shown in Fig. 5.

3.2. Delignification

Delignification was carried out during pulping and liquefaction processes. The results of delignification show that the residue and dissolved parts differ from one process to another. From the obtained results (Table 1), it was found that in the liquefaction process the undissolved part was 25%. It was mainly silica and ash; while the undissolved part in the pulping process was 50% and it was composed of cellulose and silica. Also, the dissolved part in the liquefaction process was composed mainly of cellulose and lignin, while in pulping process was lignin only.

3.3. Carboxymethyl cellulose (CMC)

3.3.1. IR spectra

The results of IR spectra are shown in Fig. 6. The spectroscopic IR data of the prepared CMC (A) and the commercial one (B) were consistent with their structural assignment. Thus, IR spectra of the samples showed identical bands. The IR spectrum of prepared CMC (Fig. 6A) showed the appearance of bands at 3432 cm^{-1} (OH-stretching), 2919 cm^{-1} (C—H), 1629 cm^{-1} (C=O), 1412 cm^{-1} (lignin component), 1186 cm^{-1} (C—O) and 1121 cm^{-1} (C—O—C).

The IR spectrum of commercial CMC (Fig. 6B) showed band at 3431 cm^{-1} (OH-stretching), 2945 cm^{-1} (C—H), 1599 cm^{-1} (C=O), 1490 cm^{-1} (lignin component), 1438 cm^{-1} (O=C—O symmetric), 1291 cm^{-1} (C—O) and 1063 cm^{-1} (C—O—C).

3.3.2. Degree of substitution (DS)

The carboxyl content of samples prepared from rice straw according to first process, second process and third process are 215, 230 and 230 mmol/100 g sample, respectively. The DS corresponding to these values of carboxyl content were calculated and found to be 0.39, 0.42 and 0.42, respectively (Table 2).

3.3.3. Solubility of CMC

Solubility of CMC samples prepared as described in the experimental section was measured. It was found that the measured solubility of the CMC samples which were prepared by the three different methods were 50%, 90% and 100%, respectively (Table 2).

3.4. X-ray analysis

X-ray diffraction patterns of the powder remained after burning rice straw and/or rice straw residues revealed that the sample contains remainate of silica formed in the form of α-quartz. Fig. 7, main diffraction lines 4.270, 3.507 (card index no. 33–1161).

According to X-ray fluorescence analysis (XRF) (Fig. 8), the silicon content (SiO_2) in the sample was about 69%.

3.5. Particle shape and size

A transmission electron microscope was used to take photographs of high magnification for identification of the particle size and shape of the remaining powder. Micrograph of the powder

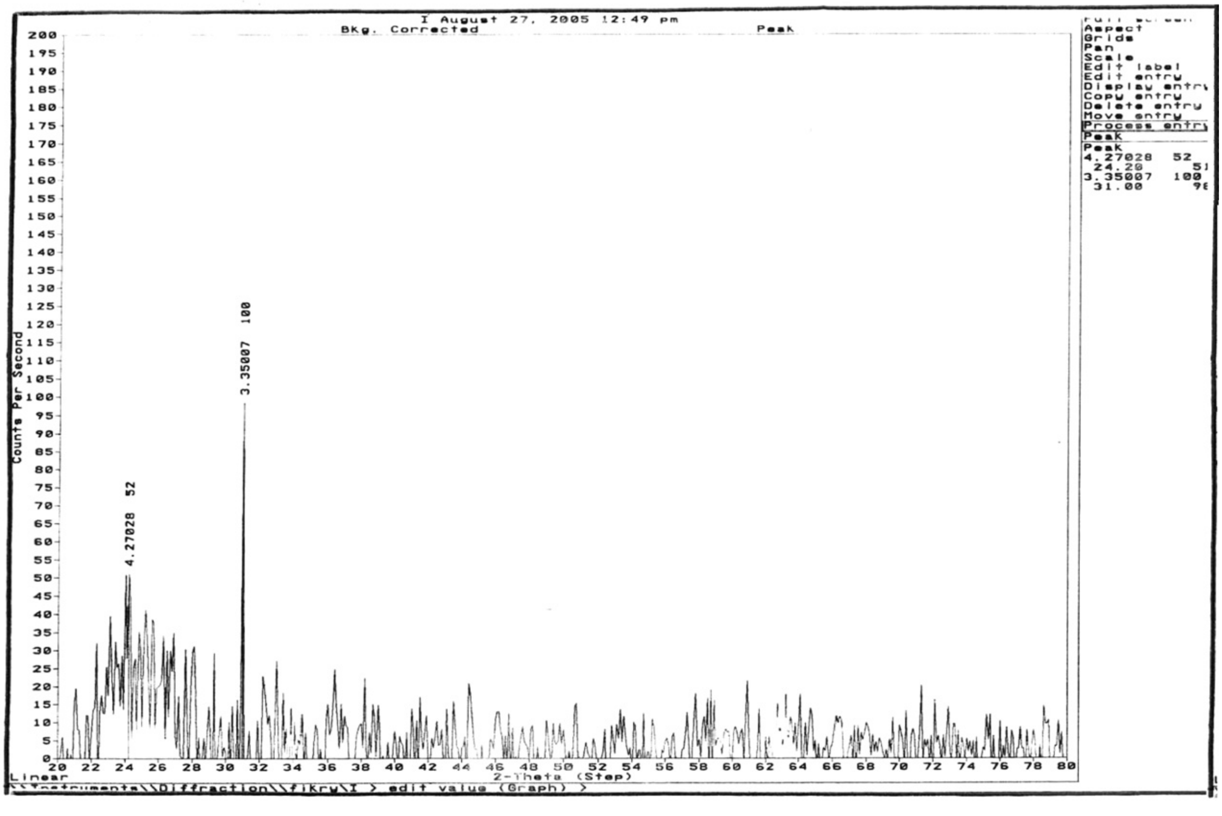


Fig. 7. X-ray diffraction pattern of remained powder after burning rice straw.

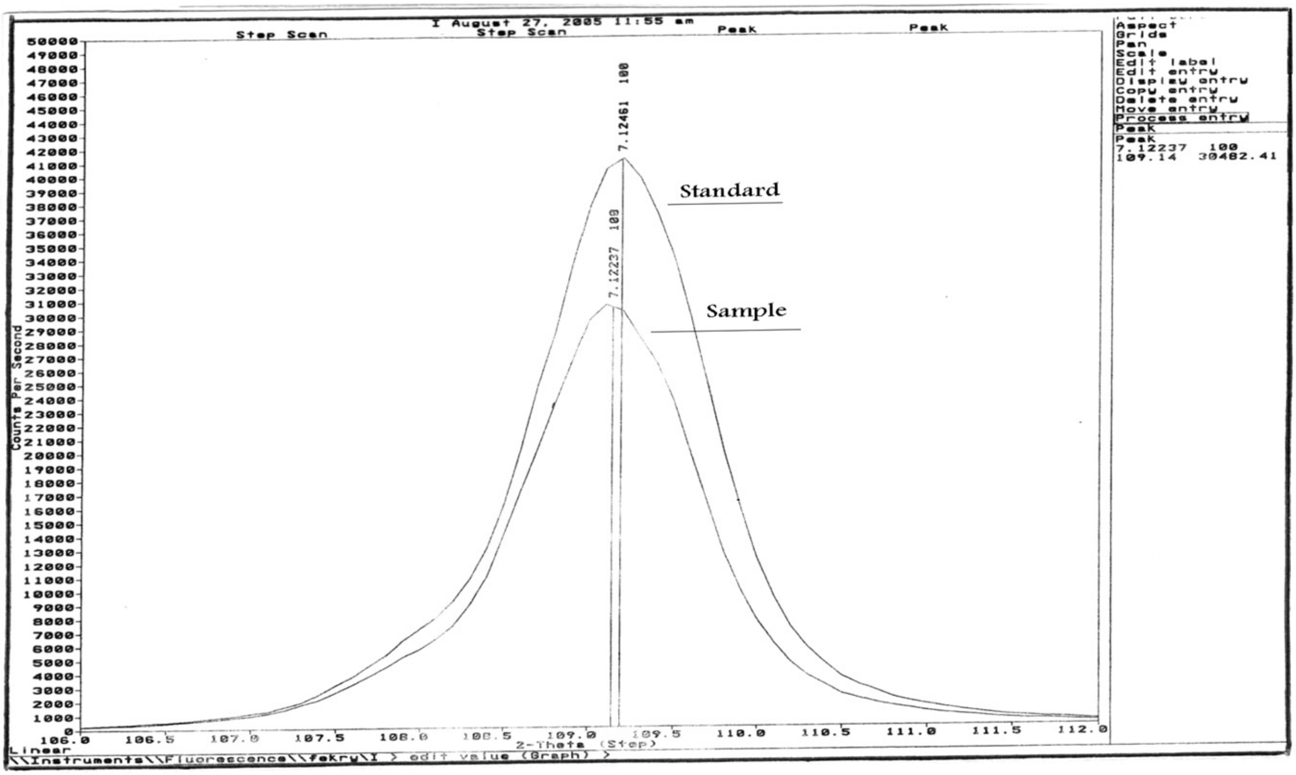


Fig. 8. X-ray fluorescence of remained powder after burning rice straw.

sample under investigation is shown in Fig. 9. The obtained particles were nearly spherical in shape with ultra fine size ranging from 18–68 nm.

3.6. Characterization and evaluation of the remained powder

Silica content in the burned samples obtained from rice straw, liquefied and pulped rice straw is shown in Table 3. Table 4 illustrates the measured characteristics of the powder under investigation. The results show suitable values of specific gravity, solubility, hydrogen ion concentration and chemical resistance, this is beside its white grayish color; these properties favor its use in wide range of applications. It is of an ultra fine particle size (18–68 nm). So it is desirable to handle it appropriately to minimize unnecessary dusting; and as it is ultra fine it does not contribute to optical properties such as brightness or hiding power (Patton, 1973). It is thought that silicon was accomplished in the structure of rice straw in a definite distribution and so it was expected to obtain it in an ultra fine form on burning (Ibrahim, Abdel-Mohsen, & Abou-Ayana, 1996).

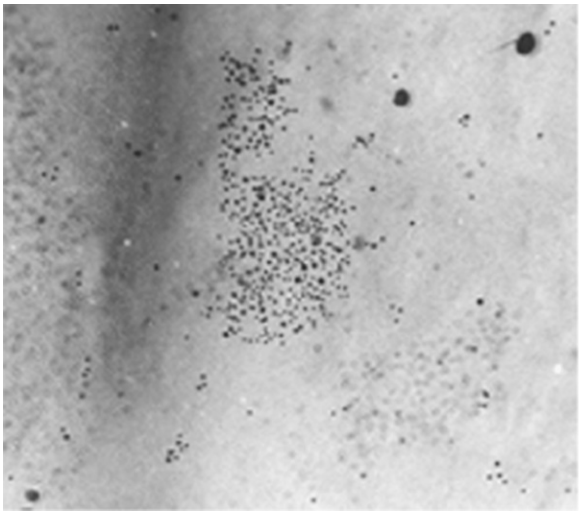


Fig. 9. Transmission electron photomicrograph of the remained powder (magnification ×126,000).

Table 3
The effect of burning on rice straw and rice straw residues

Sample	Rice straw (g)	Residue-(g)	Ash content (silica) %
Rice straw	100		17.95
Residue after liquefaction process	100	25	1.5
Pulped rice straw	100	50	5.18

Table 4
Characteristics of the retained powder

Appearance	White grayish ultra fine powder
Particle shape	Nearly spherical
Particle size	18–68 nm
Oil absorption (g/100 g)	33
Specific gravity	2–2.1 g/cm^3
Bulking value (gal/100b)	0.06
Moisture content	Nearly free of water
Matter soluble in water at room temp. (g/100 ml)	Insoluble
pH of the extract Solution	7 ± 0.1
Bleed resistance	Excellent
Acid resistance	Excellent
Alkali resistance	Excellent

Table 5
Dry film composition – by weight – of the formulated paint films

Composition	Formula number											
	1	2	3	4	5	6	7	8	9	10	11	12
Silica fume	30	–	25	20	10	–	60	–	–	20	20	20
Quartz	–	30	–	–	–	–	–	60	–	–	–	–
Prepared silica	–	–	5	10	20	30	–	–	60	16.7	16.7	16.7
China clay	20	20	20	20	20	20	–	–	–	20	20	20
Baryte	10	10	10	10	10	10	–	–	–	10	10	10
Total pigment	60	60	60	60	60	60	60	60	60	66.7	66.7	66.7
Medium alkyd resin	36	36	36	36	36	36	36	36	36	30	–	–
Butylated melamine resin	4	4	4	4	4	4	4	4	4	3.3	–	–
Chlorinated rubber	–	–	–	–	–	–	–	–	–	–	–	25
Chlorinated paraffin	–	–	–	–	–	–	–	–	–	–	–	8.3
Epoxy resin	–	–	–	–	–	–	–	–	–	–	25	–
Hardener	–	–	–	–	–	–	–	–	–	–	8.3	–
Total binder	40	40	40	40	40	40	40	40	40	33.3	33.3	33.3
P/B ratio	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	2	2	2

Table 6
Physical, mechanical and chemical test data of the formulated paint films

Test	Formula number											
	1	2	3	4	5	6	7	8	9	10	11	12
Adhesion[*]	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0	Gt0
Hardness[**]	91	82	94	93	94	94	77	82	104	96	100	131
Ductility[***]	6.0	6.4	6.0	6.2	6.1	6.2	6.4	6.4	6.4	5.4	6.1	6.2
Acid resistance	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
Alkali resistance	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Pass	Pass

[*] Gt0 indicates that the cut edges are completely smooth and no part of the coating has been chipped off and Gt4 refers that the coating has chipped off (along the cut edges) in wide strips and the chipped off area is about 65% or more.

[**] The damping of the pendulum will increase with increasing softness of the coating to be tested. The reference value is the time in seconds expressed as a damping period, which the pendulum requires to slow down from the initial value to a lower value.

[***] Ductility (deformability) of a coat film determines the depth of a dent (mm) in the coating system at which the coating tears or flakes.

3.7. Application of the remained powder in paint formulations

The characterized and evaluated powder under investigation was studied as an extender pigment by incorporating it in some paint formulations. Twelve paint formulations were laboratory prepared; the composition of these paints is given in Table 5. The results of the physico-mechanical and chemical properties of these paints are given in Table 6. Examination of the test results of paint films No. 1 & 2 that are of the same composition and differ only in the type of the silica contained, it is clear that, the film of paint No. 1 containing amorphous silica fume was of higher hardness while slight higher ductility was recorded for paint film No. 2 containing crystalline quartz.

Test results in Table 6 show that using 5–30 percent by weight of the prepared powder in the formulated paints gave films of nearly the same or slightly higher hardness and ductility in comparison with that obtained on using silica fume paint No. 1 & 3–6 while they record noted higher film hardness and slight lower ductility in comparison with paint No. 2 containing quartz.

Results of paint films No. 7, 8 and 9 show that depending on silica fume, quartz and the prepared powder respectively as a sole pigment in these paints, using the same binding medium and the same pigment/binder ratio gave rise to paint films of the same ductility but they markedly differ in hardness. Marked height in the film hardness was recorded for paint film containing the pigment under investigation. This may be attributed to its specific ultra fine particles of the nano-size.

The test results of paints No. 4 & 10 show that the increase of the pigment/binder ratio (P/B) by increasing the content of the pigment under investigation, no clear increase was recorded for the film hardness but noticeable decrease in ductility was recorded. On the other hand, the results of paint films No. 10, 11 & 12 show that high film hardness and high ductility were obtained when the pigment under investigation was incorporated in the paint based on chlorinated rubber and reasonable values were obtained when alkyd-butylated melamine resin and epoxy resin were used respectively.

4. Conclusion

Conclusions arrived of from these studies are given below:

- Preparation of carboxymethyl cellulose (CMC) as a beneficial material from rice straw by chemical methods to overcome an environment problem happened by burning of the rice straw in the field at harvest time.
- White grayish ultra fine powder of nano particle size was obtained on burning rice straw or the residues obtained after liquefaction process of rice straw at 550 °C. It was mainly silica and it can be successfully used in paint formulations as extender pigment. It rendered the paint film hard, and extremely hard when used as a sole pigment while keeping it of reasonable ductility, this was in comparison with some other types of silica.

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