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Rice straw as a new resource for some beneficial uses

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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)

$$\text{Cell–OH} + \text{NaOH} + \text{ClCH}_2\text{COONa} \rightarrow \text{Cell–O—CH}_2\text{COONa} + \text{NaCl} + \text{H}_2\text{O}.$$

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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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. Deligninification/pulping

Deligninification 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:

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

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

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.