RESEARCH ARTICLE

Characterization of Rice Husk for Sustainable Applications

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ABSTRACT

Paddy (*Oryza sativa* L.) is the third major crop grown in the world. Paddy consists of 70-75 per cent rice, 18-22 per cent husk and 5-8 per cent bran. Husk obtained from milling industry is mostly burnt or dumped as waste in the open fields. Physical properties, proximate analysis and biochemical analysis were done in the current study for analyzing the feasible methods for utilization of rice husk. The combined hemicellulose and cellulose content of 53.45 per cent in the husk indicates its potential usage in the paper pulp industry. Volatile content (71.23 per cent) of rice husk proposes its promising applications as fuel for the gasifier. Lignin content (26.20 per cent) in rice husk marks it as viable biomass for char yield. Ash content of rice husk was found to be about 20 per cent which predominantly contains silica. The higher silica content of rice husk ash suggests its usage on the preparation of diode cells and battery electrodes.

Keywords*: Rice husk, rice husk ash,silica*

INTRODUCTION

Rice is the staple food for more than half the world population. It is an important commodity in South and South-East Asia as about 90 per cent of world rice production is from this region (Sangavi*et al.*, 2018). Rice plays a major role in the Indian economy and hence occupies a central position in agricultural policy-making of India (Dangwal*et al.*, 2011). The yield of Rice in India was approximately found to be 111.01 million tonnes for the year of 2017-18. About 20 per cent of which is rice husk approximating 22.20 million tonnes yield of Rice Husk (Ministry of Agriculture & Farmers Welfare, 2018).

The products of rice milling industries are rice, bran and husk. Bran is processed to make oil. Rice husk is the hard covering of paddy seed which protects the seeds from physical damage and attacks of insects and pathogens. Husk obtained from milling industry is mostly burnt or dumped as waste in the open fields. Rice husk though is a potential material for value addition, it is mostly used in boilers as fuel.

Rice husk is rarely used as animal feed due to its lower nutritive quality. It is underused as fuel for cooking and in boilers as continuous usage of rice husk leads to the formation of scales in the heating equipment. Rice husk seems a viable option for the production of biocharonly in smaller scales. Studies are yet being carried out to utilize rice husk for energy generation, silica production and composting .

The physical and chemical characterization of the rice husk plays a vital role in determining the feasible process for effective utilization of rice husk (Shen, 2017). Further, incineration of rice husk produces about 20per cent ash which contains 85-90 per cent silica. Temperature and time play a vital role in the composition of rice husk ash. The percentage of silica obtained is reported to be of use in the ceramics industry, cement industry, aerogels and zeolites (Ugheoke*et al.*, 2012). Though usage of rice husk has been the research focus for decades, very minimal data on the characteristics of rice husk are available. The current study is carried out to understand the composition of rice husk which would be helpful in determining the feasible process for utilization of rice husk.

MATERIAL AND METHODS

Rice husk analyzed was obtained as the milled by-product from Kurnool district from Andhra Pradesh, India. The physical property, proximate and biochemical analysis was carried out for quantitative analysis of rice husk. The Thermo Gravimetric Analysis (TGA), Scanning Electron Microscope (SEM) analysis, Electron Diffraction Spectroscopy (EDS) and X-Ray Diffraction (XRD) analysis were further carried out for qualitative analysis of rice husk.

I. Physical properties

The dimensions, bulk density and moisture content of rice husk werefound to understand the physical properties of rice husk using the following methodologies:

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a)Dimensions

The dimensions of unbroken rice husk were measured. The length, width and thickness of rice husk were measured using a micrometer screw gaugeand the average of each was calculated. The length was measured between the two tips of the rice husk.The width was taken to be the longest perpendicular to the length. Thickness was measured between the two flat faces of the husk.

b)Bulk density

Bulk density was determined (ASTM D6683 -14) by filling the vessel of known volume with rice husk. The rice husk was then weighed ($wt._{bd}$) and bulk density was calculated as per equation (1).

$$\text{Bulk density}(\rho_b), kgm^{-3} = \frac{wt._{bd}}{\text{Volume of vessel}} \quad (1)$$

c) Moisture content

Moisture content (MC) of rice husk was found by oven-dry method (ASTM, E-87). Sample to be characterized was taken and its weight was noted (w_i). The sample was kept in a hot air oven at 1053°C until the constant weight of the sample was achieved. The final weight of the sample was noted down(w_f). Moisture content in wet basis (wb) and dry basis (db) of the sample was estimated as per equation (2) and (3).

$$MC\% \, (wb) = \frac{(w_i - w_f)}{w_i} \times 100 \quad (2)$$

$$MC\% \, (db) = \frac{MC\,(wb)}{(100 - MC\,(wb))} \times 100 \quad (3)$$

A proximate composition such as volatile matter, ash content and fixed carbon of rice husk was found using ASTM procedures as given below. Volatile matters are those compounds in rice husk which have a low melting point. The volatiles can hence be used for harnessing of energy. Fixed carbon is the residual carbon remaining after the devolatilizationprocess of the sample.

a.Volatile Matter

A known weight of dried rice husk was taken in a closed silica crucible and kept at 650°C for six minutes and at 750°C for six minutes (ASTM, E-872). The volatile matter was found as per equation (4).

$$\text{Volatile matter}, \% = \frac{\text{Loss in wt. of the sample,g}}{\text{wt. of dried sample,g}} \times 100$$

b.Ash Content

The ash content of rice husk was found out (ASTM, E-830) by taking a known quantity of dried sample in an open crucible and subjecting it to 750°C until a constant weight was reached. The ash content was then estimated as per equation (5).

$$\text{Ash content},\% = \frac{\text{wt. of ash formed,g}}{\text{wt. of dried sample,g}} \times 100 \quad (5)$$

c.Fixed Carbon

The fixed carbon of dried biomass sample was calculated by subtracting the sum of volatile matter (VM) and ash content from 100 as given in equation (6).

$$\text{Fixed carbon}, \% = 100 - (VM(\%) + ash(\%)) \quad (6)$$

III. Biochemical analysis

The structural property of the rice husk viz. cellulose, hemicellulose and lignin were found to study its influence onthermo chemical conversion (Raveendran et al, 1995). NREC method was used for the determination of cellulose, hemicellulose and lignin content of selected biomaterials are described in the following section.

i) Extractives

1g of the rice husk sample was taken in a drum bottle (w_{ei}). 60ml of acetone was added to the sample and kept in a water bath at 90°C from 2 h. The solution was then cooled to room temperature and filtered through Whatman paper grade 42. The residue was washed using distill water until the colour disappears. The filtrate was incubated at 403°C until a constant weight was reached (w_{ef}). Percentage extractives were calculated as per equation (7).

$$\text{Extractives}, \% = \frac{(w_{ef} - w_{ei})}{w_{ei}} \times 100 \quad (7)$$

iii) Hemicellulose

1g of the oven-dried rice husk sample was taken in a test tube (w_s) and 10ml of 0.5M NaOH was added to the sample. The sample was kept in the water bath at 80°C for 3h. The sample was allowed to reach the room temperature and the solution was filtered through Whatman grade 42 paper. The sample (w_{hi}) was dried in a hot air oven at 105°C until the sample reached constant weight (w_{hf}). Hemicellulose content was calculated as per equation (8).

$$\text{Hemicellulose}, \% = \frac{(w_{hi} - w_{hf})}{w_s} \times 100$$

iii) Lignin content

300mg of oven dried rice husk sample (w_{ls}) was taken with 3ml of 72 per cent sulfuric acid in a Duran bottle. Incubation of the sample was done for 60min while the sample was being stirred every 5min. The sulfuric acid in the incubated solution was diluted to 4% after the incubation time. The sample was then sealed and autoclaved for 1 h at 121°C. After completion of the autoclave cycle, the hydrolysates were cooled slowly to reach the room temperature.

The solution was filtered through Whatman grade 42 paper. The collected filtrate was added with calcium carbonate to neutralize the solution. This solution was used for determining acid soluble lignin by using UV-VIS spectrophotometry. The residue from filtration was dried at 1053°C in hot air oven until a constant weight was reached. The dried insoluble residue was incinerated at 75025°C for 2 h. The calculation for lignin content was done as per equations 9 to 16.

$$\text{Oven Dry Weight (ODW) of extractives free sample, } \% = \frac{\text{wt. (air dry sample) x \% TS}}{100} \quad (9)$$

$$\text{Acid insoluble residue (AIR), } \% = [\frac{\text{wt. (residue)}}{\text{ODW}}] \text{ x } 100 \quad (10)$$

$$\text{Acid insoluble lignin (AIL), } \% = \{\frac{\text{wt. (residue) - wt. (ash) - wt. (protein)}}{\text{ODW}}\} \text{ x } 100 \quad (11)$$

where,

$$\text{wt, (protein)} = \text{amount of protein in acid soluble residue} \quad (12)$$

$$\text{Acid soluble lignin (ASL), } \% = \frac{\text{(UV (abs) x volume (filtrate) x dilution)}}{(\varepsilon \text{ x ODW x pathlength})} \text{ x } 100 \quad (13)$$

$$\text{Dilution} = \frac{\text{(volume (sample) x volume(diluting sample))}}{\text{volume (sample)}} \quad (14)$$

$$\text{where, } \varepsilon = \text{Absortivity of biomass at specific wavelength} \quad (15)$$

$$\%\text{lignin (extractive free)} = \%\text{ AIL} + \%\text{ ASL} \quad (16)$$

iv) Cellulose content

The cellulose content of biomass samples was calculated as follows:

$$\text{Cellulose content}(\%) = 100 - [\text{M.C}(\%) + \text{hemicellulose}(\%) + \text{lignin}(\%) + \text{ash content}(\%)] \quad (18)$$

IV. Thermogravimetric Analysis (TGA):

To understand the nature of thermal degradation of rice husk in inert (nitrogen) atmosphere, TGA analysis was carried out. TGA was done using Thermogravimetricanalyzer (TA instruments, India – Model: TGA Q50) coupled with a data processor. The heating rate was given at 20°C/min.

V. Scanning Electron Microscope - Electron Diffraction Spectroscopy (SEM-EDS):

The thermal degradation of rice husk resulted in the formation of black rice husk ash. To know the constituents of the ash, EDS was used. The morphological and compositional characters of rice husk ash wereanalyzedusing SEM-TESCAN, VEGA LSU.

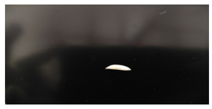
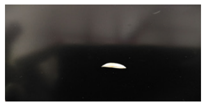
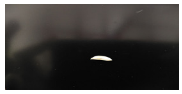
VI. X-ray Diffraction (XRD) analysis

XRD analysis was done to understand the compound form of elements present in the rice husk ash and its structural characteristic. This was carried out in XRD-PHILLIPS XPERT PRO, in NFTDC (Non-Ferrous materials Technology Development Center) in Hyderabad, India. The sample was measured at 25°C by continuous scan method.

RESULTS AND DISCUSSION

Rice husk is found to have two leaf-like structures called the lemma and palea(Zou, 2019). The average dimensions of rice husk are given in Table 1. The bulk density of undried rice husk was found to be 120kg/m^3. It is also found that the bulk density of rice husk increased with the increasein moisture content.

Table 1. Dimensions of rice husk

Property	values (mm)	Depiction
Length	8.00-9.00	
Breadth	2.50-3.00	
Thickness	0.10-0.15	

Moisture content (wb) of the rice husk was found to be 8.64per cent. The proximate analysis of rice husk showed the average volatile content of 71.23per cent. The ash content of rice husk varied between 18 and 21.4 per cent. The fixed carbon in the rice husk ash was 7.3 per cent.

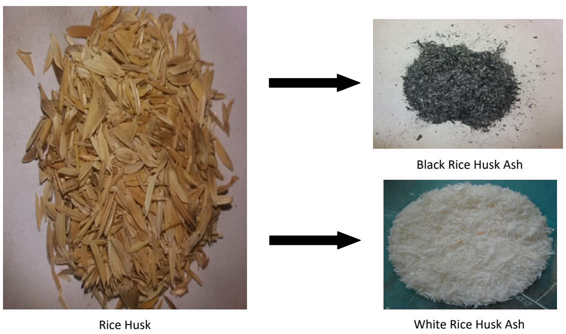


Plate 1. Products of rice husk incineration

The extractives present in rice husk accounted to 11.71per cent.The chemical components of rice husk were consisting of 23.33 per cent of hemicellulose, 30.12 per cent of cellulose and 26.20 per cent of lignin.

The results show that the rice husk has a higher percentage of lignin (26.20 per cent)which shows a capable application of rice husk to produce char.

The minerals (potassium and calcium as observed in the EDS results) present in the rice husk acts as a catalyst in lowering the pyrolysis temperature.The volatile pyrolysis products (fresh char) is highly reactive in nature. $CO_2$and H_2O, which are the primary products of pyrolysis after devolatilization, react with char in the presence of a catalyst to produce CO and H_2. This leads to the reduced yield of char when rice husk is used for pyrolysis.

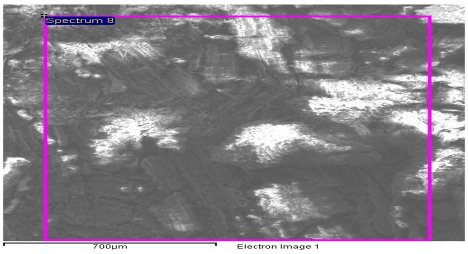


Plate 2. SEM image of rice husk ash

Demineralization of rice husk before feeding it for pyrolysis process would though ensure a higher yield of char. This is the cause, the catalyst action would become a lesser and higher percentage of lignin leads to higher char yield(due to the aromatic structure and chains present in lignin). This can be explained asa methoxyl group present in lignin decompose to stabilize the large molecule fragments and prevent the polymerization of char.(Wang *et al.,* 2017). The presence of higher percentage volatiles though can be of use for gasification, but reports of scaling due to high ash content in rice husk have been of concern.

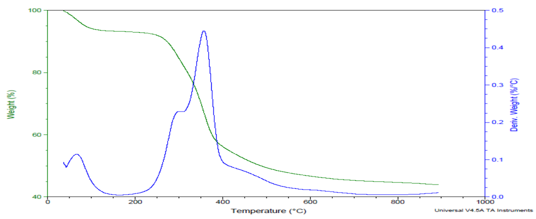


Figure 1. TGA graph of rice husk

The combined percentage of cellulose and hemicellulose (53.45) shows the potential of rice husk as biofuel and raw material in paper and pulp industry. Due to the higher lignincontent, rice husk becomes a poor nutritional material to be used as animal feed. It can though be used for making of activated carbon that can be used for removal of heavy metals from dyes once pretreated.

Figure 1.represents the thermal degradation of rice husk at the inert atmosphere. Weight loss upto 110°C attributes to the removal of moisture content from the rice husk. The maximum weight loss was observed from 250 to 400°C represented evolatilization. The weight loss occurred from 400 to 500°C attribute to the degradation of hemicellulose and cellulose. The weight loss beyond 600°C represented the degradation of lignin in the sample.

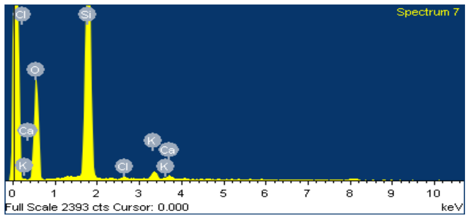


Figure 2. EDS analysis results of rice husk ash

The thermal degradation of rice husk at the inert atmosphere lead to the formation of black rice husk residue due to the presence of fixed carbon. The ash obtained after incineration resulted in white rice husk ash as a product. Further, black rice husk residue was obtained until the temperature of 400°C and white rice husk were obtained above the temperature of 400°C. The volatiles and fixed carbonin the rice huskis slowly lost during the incineration at a temperature above 400°C leaving silicates in rice husk as primary residue.

Rice Husk is exceptional biomass containing a higher percentage of ash (maximum 25 per cent (Singh, 2018)). Rice husk ash is more of a pollutant to the soil. This is because rice husk ash obtained from uncontrolled combustion (temperature exceeding 700°C) starts to form significant amounts of crystalline minerals which are non-reactive and takes longer to degrade. This alsotends to significantly disturb the pH of the soil. The rice husk ash also forms deposits when rice husk is used as fuel in boilers or for gasification.

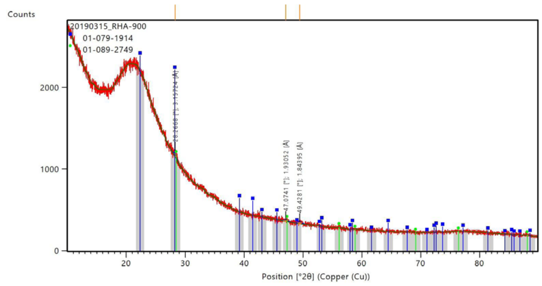


Figure 3. XRD analysis of rice husk ash

To understand the nature of rice husk ash, SEM-EDS analysis was caried out. The results showed that the ash contained 76.53 per cent silica (SiO_2). 20.51 per cent of the other metallic impurities was that of calcium, potassium and magnesium(Figure 2). The whiteness of the ash reflects the presence of silica. The SEM image given in Plate 2 shows the microporous cellular structure of the rice husk ash. The porous property of the ash explains the higher absorption tendency which makes the rice husk viable for usage in high mineral or oil absorption.

The XRD analysis (Figure 3.) indicatedthe components present in the rice husk ash. The peaksof at 28θ, 47.07° and 49.43° matchedwith the standard diffraction pattern of SiO_2. The absolute intensity of the highest peak was found to be79.03counts per second.The subsequently labeled peaks register with the standard peaks of SiO_2. The hump instead of a sharp peak in the graph indicate the SiO_2 being inan amorphous state. Amorphous silica has higher workability than the crystalline silica. These results showthe possibility of wide applications of rice husk for extracting amorphous silica which is of great use in steel industries (Kumar *etal.,* 2012), ceramics industry(Sobrosa *et al.*, 2017), brick industry, silica derived Rice nanomaterials (Chu*et al.*, 2018) and cement industry (Abbas *et al.,* 2019). The flexibility in handling and treating of SiO_2 obtained given its amorphous nature is an added advantage for the utilization of rice husk derived SiO_2(Larbi *et al.,* 2011). This shows the potential use of rice husk as a valuable product instead of burning in the open field.

CONCLUSION

In the present scenario, most of the rice husk is underutilized. This is due to poor nutritive value, low bulk density, a higher amount of volatiles and silica which makes it tough for the bacterial decomposition of rice husk. Further, a vast amount of rice husk ash is produced due to the burning of ricehusk which becomes a source of pollution.The presence of 53.45 per cent of combined hemicellulose and cellulose content in rice husk makes it viable raw material in biofuel and paper pulp industries. Rice husk can be efficiently used as fuel for pyrolysis when demineralized. Further, it can be used as fuel for boilers and in gasification at smaller scales. Rice husk ash is found to have the maximum amount of silica concentration comparing to any biomass. The presence of carbon and silica in rice husk marks it a valuable product in the manufacturing of silica/carbon or silicon/carbon products. The silica from rice husk ash can also be used as a fertilizer additive for soil application. It is of higher value in the ceramics industry and as a filler for pozzalian cement and rubber due to the silica present in rice husk. The silica from rice husk will also be useful in the field of nanotechnology for making of silica nanospheres for the absorption of other minerals. The study could be of use for understanding the characteristics of rice husk for its utilization as a valuable natural resource.

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