

Full Length Research Paper

Elemental analysis of rice husk ash using X – ray fluorescence technique

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Rice husk ash is one of the most silica rich raw materials containing about 90 – 98% silica after complete combustion among the family of other agro wastes. Ash samples from rice husks of five different origins were prepared at two different temperatures, 500 and 1000°C, respectively and the ash content was evaluated at each temperature. The interestingly high percentage of silica (taking up from the soil during paddy growth) in rice husk ash which has various industrial and domestic applications necessitated the process of determining the presence and amount of impurities or trace elements in ash taking up from the soil during paddy growth. Small quantities of impurities present at concentrations below one part per billion can have a significant effect on the quality of devices constructed from the silica obtained from the ash. The X – Ray Fluorescence (XRF) technique was used to analyze each sample heated to a temperature of 1000°C at which excellent chemical activity could be exhibited to characterize the ash in terms of the purity of the silica level by the determination of the trace (impurity) elements present that has a nature that can determine their removal method to get the pure silica. The result of the XRF showed that rice husk ash (RHA) had a very low impurity concentration of 1.1 (sample 1) to 5.58% (sample 4) corresponding to 98.9% (sample 1) and 94.42% (sample 4) purity level of silica indicating that rice husk which is an agricultural waste is a potential source of silica with a high purity level of 94 - 98.9%.

Key words: Rice husk, ash composition, fluorescence, impurity, silica.

INTRODUCTION

Rice husks are the natural sheaths that form on rice grains during their growth. Removed during the refining of rice, these have no commercial interest however can be made useful through a variety of thermochemical conversion process. The major compounds from rice husks are silica and cellulose which yields carbon when thermally decomposed (Adylov et al., 2003). On the majority of rice producing countries much of the husks produced from the processing of rice is either burnt or dumped as a waste.

Rice husk is unusually high in ash compared to other biomass fuels – close to 20% (Adylov et al., 2003). The ash is 92 – 95% silica, highly porous and light weight, with a very external surface area. With such a large ash content and silica content in the ash it becomes economical to extract silica from ash which takes care of ash

Rice husk ash (RHA) is a term describing all types of ash produce from burning rice husks which vary considerably according to burning techniques. The silica in the ash undergoes structural transformations depending on conditions (time, temperature etc) of combustion. At 550 to 800°C amorphous ash is formed and at temperature greater than this, crystalline ash is formed (Joseph et al., 1989). The change from amorphous to crystalline ash occurs at approximately 800°C, although the process is often 'incomplete' until 900°C is achieved (Sugita, 1993). All the combustion processes devised to burn rice husks remain below 1440°C, which is the rice husk melting point (Sugita, 1993). The rice husk ash obtained at 1000°C will exhibit excellent chemical activities and will be white in colour (Sugita, 1993).

These types of silica have different properties and it is important to produce ash of the correct specification for the particular end use.

Rice husk ash has so many applications due to its various properties.

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Uses of rice husk

Rice husk ash is used by the steel industry in the production of high quality flat steel used for automotive body panels (Sugita, 1993).

It is an active pozzolan which when combined with lime in the presence of water results in a stable and more amorphous hydrate (calcium silicate). This is stronger, less permeable and more resistant to chemical attack (Owens, 1999).

Due to its insulating properties, RHA has been used in the manufacture of refractory bricks. Refractory bricks are used in furnaces which are exposed to extreme temperatures, such as in blast furnaces used for producing molten iron and in the production of cement clinker.

There is anecdotal evidence of RHA being used in the manufacture of lightweight insulating boards in developing countries (Owens, 1999).

The Indian Space Research Organization has successfully developed technology for producing high purity precipitated silica from RHA and this has a potential use in the computer industry. Consortiums of American and Brazilian scientists have also developed ways to extract and purify silicon with the aim of using it in semiconductor manufacture. A company in Michigan is purifying RHA into silica suitable for several industries, including silicon chip manufacture.

It is against these points that XRF method is to be used in identifying how pure RHA is in terms of silica by determining the impurity level or concentration of the ash produce from the rice husk.

Global rice production

Rice is grown on every continent except Antarctica and covers 1% of the earth's surface. It is a primary source of food for billions of people, and ranks second to wheat in terms of area and production (FAO, 2002). During growth, rice plants absorb silica from the soil and accumulate it into their structures. It is this silica, concentrated by burning at high temperatures removing other elements, which makes the ash valuable.

The annual production of paddy rice globally was 579,500,000 tonnes in 2002 (FAO, 2002). Of this, 95% was produced by 20 countries of which Nigeria is the 17th position. Production of rice is dominated by Asia, where rice is the only food crop that can be grown during the rainy season in the waterlogged tropical areas.

Yields are affected by several factors, including the agronomy of the crop, the physical and cultural environments and scale under which the rice is grown. International Co-ordination and Co-operation in technological advances of rice production is providing alternatives to the limitations of cultural practices, by the use of chemical fertilizers, insecticides, pesticides and introduction of new varieties. Rice production is often set back by the weather, monsoons and droughts, but the effects of these are

increasingly being limited by irrigation and water control systems (Velupillai et al., 1997).

The chemical properties of ash arising from rice husks are thought to vary from region. The differences have been attributed to the conditions under which the paddy is grown, such as climate, soil, and use of fertilizers.

Factors influencing the use of rice husk

Although the potential global estimate of Rice Husk Ash (RHA) production is 21,000,000 tonnes, the actual scope for utilization is considerably less. The majorities of mills from which the husks are sourced are small and dispersed within developing countries like Nigeria. This makes collection of the resource logistically problematical, and currently husks are dumped and burnt in open piles.

In developed countries, where the mills are typically larger, disposal of the husks is a big problem. Burning in open piles is not acceptable on environmental grounds, and so the majority of husk is currently going into landfill.

X-ray fluorescence (XRF)

X-ray fluorescence, XRF is the emission of characteristic "secondary" (or fluorescent) x-rays from a material that has been excited by bombarding with high energy x-rays or gamma rays.

XRF technology provides one of the simplest, most accurate and most economic analytical methods for the determination of the chemical composition of many types of materials, particularly in the investigation of metals, glass, ceramics and building materials, and for research in geochemistry, forensic science and archaeology. It is non-destructive and reliable, requires no, or very little, sample preparation and is suitable for solid, liquid and powdered samples (John et al., 2001). It can be used for wide range of elements and provide detection limits at the sub-ppm level; it can also measure concentrations of up to 100% easily and simultaneously (Jenkins, 1999).

Theory of X-ray fluorescence

The X-ray fluorescence principle is shown in Figure 1. An inner shell electron is excited by an incident photon in the X-ray region. During the de-excitation process, an electron is moving from a higher energy level to fill the vacancy. The energy difference between the two shells appears as an X-ray, emitted by the atom. The X-ray spectrum acquired during the above process reveals a number of characteristic peaks. The energy of the peaks leads to the identification of the elements present in the sample (qualitative analysis), while the peak intensity provides the relevant or absolute elemental concentration (semi-quantitative or quantitative analysis) (Loupilov et al., 2001).

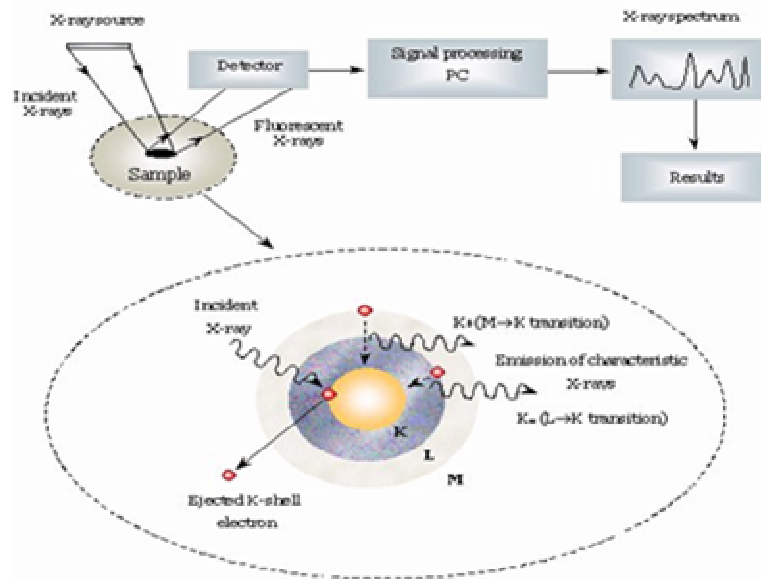


Figure 1. The principle of XRF and the typical XRF detection arrangement.

Appendix I. Radioisotopes commonly used in XRF arrangements.

Isotope	Half-life	Radiation	Energy (keV)	Excited elements
Fe-55	2.7 y	Mn K	5.9	Al-Cr
Co-57	270 d	Fe K	6.4	<Cf
		γ	14.4	
		γ	122	
Cd-109	1.3 y	Ag K	22.2	Ca-Tc
		γ	88	W-U
		γ	136	
Am-241	470 y	Np L	14-21	Sn-Tm
		γ	26	

A typical XRF spectroscopy arrangement (Figure 1) includes a source of primary radiation (usually a radioisotope or an X-ray tube) and equipment for detecting the secondary X-rays (Omote et al., 1995).

When materials are exposed to short wavelength x-rays or to gamma rays, ionization of their component atoms may take place. If an x-ray beam is used to excite atoms in a sample, electrons near the nucleus emit secondary fluorescent x-rays on reversion to their original states. Short wavelength x-rays are sorted by diffraction in a pure analyzing crystal of known d-spacing. Since

$$n\lambda = 2d \sin \theta - \text{Bragg's law, } \theta \text{ can be set to a}$$

value and radiation detected for a unique wavelength characteristic of the element being analyzed, the intensity of the radiation measured, relative to a standard, is proportional to the concentration of the element (Beckhoff et al., 2006).

The irradiation of a sample is usually performed by radioisotope sources or X-ray tubes. The energy of the primary radiation should be higher than, but close to the binding energy of the K- and L-shell electrons of the excited atom (Uhlig et al., 1999).

The most widespread radioisotope sources include Fe-55, Co-57, Cd-109 and Am-241. These sources emit X-rays of definite energy, therefore being capable of efficiently exciting a limited number of atoms (Appendix I). As a result, to analyze a broad range of elements, a combination of radioisotope sources is necessary (Omote et al., 1995).

Alternatively, X-ray tubes may be used to excite the sample with characteristic or continuum X-rays. Depending on the elements to be analyzed, the anode material of the tube is selected (Appendix II).

MATERIALS AND METHODS

Five samples of the rice husks were obtained each from different

Appendix II. Specifications of some X-ray tubes.

Anode material	Voltage (kV)	Current (mA)	Excited elements
Ca (K-rays)	8-10	0.1-1	P, S, Cl
Pd (L-rays)	3-5	0.1-1	P, S, Cl
Pd (K-rays)	35	0.1-1	K-Sn (K-rays), Cd-U (L-rays)
Ti (K-rays)	10	0.1-1	Cl, K, Ca
Mo (K-rays)	30	0.1-1	K-Y (K-rays), Cd-U (L-rays)
W	35	0.1-1	K-Sn (K-rays), Tb-U (L-rays)
W	50	0.1-1	Zn-Ba (K-rays), Tb-U (L-rays)

Table 1. Ash composition at temperature T = 500°C and 1000°C.

Sample	Mass of husk (g)	Mass of ash (g) at T = 500°C	Mass of ash (g) at T = 1000°C
1	100	20.96	16.26
2	100	26.80	22.65
3	100	23.74	18.85
4	100	21.56	17.95
5	100	22.98	19.47

rice milling stations in Benue and Kogi States known to be rice producers in the middle belt region of Nigeria.

Samples 1, 2 and 3 were sourced from Ibaji, Bassa, and Ajaokuta in Kogi State while samples 4 and 5 were sourced from Markudi and Nakka in Benue State.

The husks were properly separated from some broken bran by sieving and winnowing. Then 100 g of each sample was weighed using an electric weighing machine. For each 100 g sample of the husk, small quantities were poured into crucibles which were later placed in the muffle furnace for combustion to a temperature of 500°C. The ash obtained at this temperature were allowed to cool in the muffle furnace for 24 – 30 h to room temperature and with the use of forceps and spatula the content of the crucibles for each sample was transferred into a pan for a re-weigh. The above processes were repeated again but the furnace was regulated to a temperature of 1000°C within 6 – 8 h.

The mass of the ash from each sample at the two temperatures (Table 1) were determined. The small size of the muffle furnace available in the laboratory limited the quantity of husk charred and the ash produced, hence the amount of silica to be obtained.

The method of XRF analysis involves keeping the geometry of the tube-sample-detector assembly constant; the sample was prepared as a flat disc, typically of diameter 20-50 mm. Samples were located at a standardized, small distance from the tube window. Because the X-ray intensity follows an inverse-square law, the tolerance for this placement and for the flatness of the surface must be very tight in order to maintain a repeatable X-ray flux. Ashes were machined to shape and finely ground and pressed into a tablet. A further reason for obtaining a flat and representative sample surface was that the secondary X-rays from lighter elements often only emit from the top few micrometers of the sample (Loupilov et al., 2001). In order to further reduce the effect of surface irregularities, the sample were usually spun at 5-20 rpm. It was necessary to ensure that the samples were sufficiently thick to absorb the entire primary beam (Beckhoff et al., 2006).

RESULTS AND DISCUSSION

The ashes obtained at 500°C were dark in colour indicating the presence of unburnt carbon, while the ones heat

ed at 1000°C were milky – white with percentages that vary from 16.3 (sample 1) to 22.65% (sample 2). This variation may be accounted for due to the difference in soil chemistry of the locations of collection and paddy variety (Real, 1996).

Thirteen elements were detected in all by the XRF method with slightly varying concentrations. The total impurity concentration of samples 2, 3, 4 and 5 is almost the same. However, sample 1 has a very low impurity concentration. This is due to the low level concentration value of the detected elements and complete absence of three elements (Nickel Ni, Iodine I, and Arsenic As). Arsenic was also absent in samples 3, 4 and 5; it is only detected in sample 2. The lowest atomic weight element detected is chlorine, Cl and this is due to the inability of the XRF technique to detecting elements lighter than sodium. XRF has been known from literature that it cannot detect low atomic elements especially those lighter than sodium (Na) due to instrumental limitations and low X – ray yields for the light elements unless background corrections and very comprehensive inter-element corrections are made (Jenkins, 1999). The calculated total percentage impurity (Table 2) vary from 1.1 (sample 1) to 5.58% (sample 4) which corresponds to 98.9 (sample 1) and 94.42% (sample 4) purity level of silica. These variations again could be due to the difference in the soil chemistry of the locations of collection of the samples, paddy varieties and type of chemical fertilizers used (Mehta, 1994; Real, 1996).

Conclusion

The low impurity level of concentration of the rice husk ash showed that it is highly rich in silica indicating

Table 2. Percentage impurity concentration level of XRF result.

Elements	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
K	0.5451	1.9044	2.4514	2.0009	2.4860
Ca	0.3070	0.9002	0.8707	0.7869	0.8425
Cr	0.0004	0.0169	0.0230	0.0312	0.0236
Mn	0.0422	0.1731	0.2041	0.2156	0.2545
Fe	0.1603	1.0836	0.7219	1.2093	0.6801
Ni	-	0.0325	0.0368	0.0422	0.0346
Cu	0.0008	0.0139	0.0220	0.0256	0.0207
Zn	0.0063	0.0312	0.0435	0.0237	0.0326
Sr	0.0057	0.0060	0.0031	0.0036	0.0047
Br	0.0010	0.0064	0.0075	0.0090	0.0102
I	-	0.2178	0.1735	0.0481	0.0439
As	-	0.0043	-	-	-
Cl	0.0298	1.1751	1.0048	1.1827	1.1348
Total impurity	1.0986	5.5654	5.5623	5.5788	5.5682
Total purity	98.9014	94.4346	94.4377	94.4212	94.4318

that rice husk ash which is an agricultural waste can be converted into a valuable product which has so many industrial and domestic applications. So, taking care of the impurity (trace) elements the valuable product can be explored thereby taking care of husk disposal as the rice husk is always being piled here and there and at times burnt in an open air.

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