International Journal of Applied Chemistry.
ISSN 0973-1792 Volume 13, Number 4 (2017) pp. 801-811

http://www.ripublication.com

Elemental Analysis of Rice Husk Using Proton-Induced X-Ray Emission (Pixe) Spectrometry

Clementina D. Igwebike-Ossi

Department of Industrial Chemistry, Faculty of Science,
Ebonyi State University, Abakaliki, Nigeria.

Abstract

Rice husks, an agro-waste is of increasing interest to researchers as bioresource for domestic and industrial applications due to its abundance, cheapness and 'renewability'. In this study, the elemental composition of rice husk was determined using the high-tech, highly sensitive and uncommon Proton-induced X-ray emission (PIXE) spectrometry. Milled rice husks, obtained from a rice mill in Abakaliki, Nigeria were first washed to remove sand and stone contaminants and then dried in an oven. The clean husks were ground to a fine powder, pressed into pellets and subjected to analysis using the PIXE technique. The results of the analysis revealed the presence of a total of thirteen elements. The elements detected and their concentrations (in %) are : Si as SiO_2 (25.82±0.024), Al (0.017±0.001), Fe (0.039± 0.001), Ca (0.088±0.002), Mg (0.135± 0.02), Na (0.03±0.01), K (0.099±0.003), P (0.666±0.023), S (0.217±0.009,), Cl (0.026±0.005), Ti (0.006±0.001), Mn (0.012±0.001) and Zn (0.001±0.000).The results showed that the predominant element in rice husks is silicon which occurs in the form of silica (SiO_2) as it was found to constitute 95% of the total elements present while the other twelve elements made up only 5%. P was present in a small quantity; Al, Fe, Ca, Mg, Na, S, K, Cl and Mn were in minute quantities while Ti and Zn were in trace quantities.

Keywords: PIXE spectrometry, rice husk, silica, elemental composition, analysis

INTRODUCTION

Rice husks (or hulls), the hard, outer protective covering of the rice grain, are generated in large quantities as agro-waste in the rice-producing areas of the world during the milling of rough rice (paddy) to obtain white rice. The ongoing revolutionary, global transition from the use of non-renewable to renewable resources due to environmental protection consideration has stimulated several research investigations into the use of rice husks as potential domestic and industrial bio-resource. Thus, rice husks have been found to be useful in several applications which include production of ethanol [1], lightweight bricks [2], particle board [3], as adsorbent [4], fertilizer production [5], fuel for power generators, domestic stoves and industrial furnaces [6, 7]. Rice husk is also a source of rice husk ash (RHA) which has also been found suitable for several industrial applications. [8-11]. Rice husk therefore presents a cheap, abundant and renewable resource which makes it attractive to researchers for various studies.

Plants absorb and accumulate silica from the soil into their systems to varying levels; 0.1-15% of their dry weight [12]. Among them monocots, such as rice, *Oryza sativa* , wheat, maize and barley are categorized as Si-accumulators due to their high silica contents (10-15%) [13]. Earlier investigations carried out to determine the chemical nature of rice husks, revealed that it contains a high proportion of lignin and about 20% of their outer surfaces are covered with silica [14] The presence of silica in rice husks was further confirmed by Bharadwaj et al [15] from the scanning electron microscopic image of a virgin rice husk particle in which he observed that the structure resembled that of a composite material with fibres composed of silica regularly interspaced in the matrix. The matrix consisted largely of cellulose, hemicelluloses and lignin which are thermo-chemically unstable and decompose on heating.

The elemental components of rice husks constitute only a fraction of its chemical composition and are often mentioned in relation with the lignocellulosic components, which include lignin, hemicellulose and cellulose. Muntohar [16] gave the chemical composition of rice husks as typically : cellulose (40-45%), lignin (25-30%), ash (15-20%) and moisture (8-15%). In another study, [17] the composition of rice husks was reported as 32.24% cellulose, 21.34% hemicelluloses, 21.44% lignin, 1.82% extractives, 8.11% water and 15.05% mineral ash, which gives the total lignocellulosic composition as 75.02%. Similarly, Daifullah *et al* [18] and Arnesto *et al* [19] presented the main constituents of rice husks as 64-74% volatile matter, 12-16 fixed carbon and 15-20% ash. However, in another study, the ash content of rice husks from different species of rice was found to be in the range of 18-25% [20] while in another report on the analysis of rice husk, Maeda *et al* [21], gave the ash content as 22-29%. Silica, in rice husks is often referred to as 'ash' because it is the residue of combustion of rice husks. The ash also contains other elemental components in small quantities. The result of the analysis of a rice husk sample from India [22] showed the elemental components (in mass fraction %) to be as follows: C (41.44), H (4.94), O (37.32), N (1.1), Si (14.66), K(0.59), Na (0.035), S (0.300, P(0.07), Ca(0.06), Fe (0.006) and Mg (0.003). Chockalingam *et al* [23] reported the presence of K, Mg, Na, Ca, Mn, Fe, B, Cu, Zn, PO_4 and NO_3 in the elemental analysis of another rice husk sample from India.

The most common types of analyses that have been carried out to determine the chemical composition of rice husks are proximate analysis, [23, 24] ultimate analysis, [23-25] and component analysis (lignocellulosic contents) [16]. Other methods that have been employed involve the conversion of rice husks to rice husk ash (RHA) and subsequent analysis of the RHA samples, using X-ray emission analytical techniques such as X-ray fluorescence (XRF) [26, 27]. In the XRF analysis of RHA samples obtained by burning rice husks from Benue and Kogi states of Nigeria thirteen elements (in the form of their oxides) were detected : K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Sr, Br, I, As, and Cl [27]. Igwebike-Ossi [28] reported the presence of fourteen elements (in the form of their oxides) in RHA but with a preponderance of Si (present as SiO_2) using the PIXE technique. The elements reported were as follows ; SiO_2 Al_2O_3 Fe_2O_3 CaO MgO Na_2O, K_2O, P_2O_5, SO_3 ClO_3, TiO_2 MnO, ZnO and Rb_2O. Another technique that has been used for RHA compositional analysis is Atomic Absorption Spectrometry (AAS) [29].

Proton-Induced X-ray emission or particle-induced X-ray emission (PIXE) spectrometry is a powerful, non-destructive, analytical technique used to determine the elemental composition of a solid, liquid, thin film and aerosol filter samples [30, 31]. It is based on the energy spectra of characteristic X-rays emitted by the de-excitation of the atoms in the sample bombarded with high energy protons (1-3 MeV) with the aid of a suitable energy dispersive detector [31]. PIXE can detect all elements, from sodium to uranium, giving a total of seventy-two elements (excluding Po, At, Fr, Ra, Ac, Pa and the inert gases [31].The use of proton beams as excitation source in PIXE offers several advantages over other X-ray techniques, the major ones being its high sensitivity for trace elements and lower atomic number elements determination as well as its higher rate of data accumulation across the entire spectrum which allows for faster analysis [31]. PIXE is capable of detecting elemental concentrations down to parts per million, however, the technology is still relatively new in wider avenues of chemical research. The greater sensitivity of PIXE is expected to give more accurate results than other analytical techniques earlier mentioned [27, 29].

The variation in the chemical composition of rice husks is due to its dependence on several factors which include soil chemistry, climatic conditions, paddy variety [32,33], use of fertilizer, type of fertilizer [34, 35], year of harvest, sample preparation and methods of analyses [20].

There is very limited information in literature on the use of the relatively new, high-tech and highly sensitive Proton-induced X-ray Emission (PIXE) spectrometry for analysis generally and for the determination of the elemental composition of rice husks, particularly. The objective of this work is therefore to determine the elements present in virgin rice husks using the PIXE analytical technique and to compare the results obtained with those earlier obtained for rice husk ash using the same technique as well as other X-ray emission analytical techniques such as X-ray Fluorescence (XRF).

MATERIALS AND METHODS

Equipment

i. Hydraulic Press
ii. 1.7 MeV Tandem Pelletron Accelerator, model 5SDH, built by the National Electrostatic Corporation (NEC), USA and acquired by the Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife, Nigeria. The accelerator is generally used for ion beam analysis (IBA) techniques, one of which is PIXE.
iii. End station for Ion beam analysis (IBA) designed and built by the Materials Research Group (MRG) at Themba Labs, Sommerset West, South Africa
iv. Canberra Si(Li) PIXE detector with 30mm^2 active area, Model ESLX30-150

Elemental Analysis of RHA using PIXE Technique

Sample preparation

The RHA samples were ground in a clean porcelain mortar to reduce the particle size and ensure a uniform distribution of the particles. The ground ash samples were then pressed into pellets using a hydraulic press before subjecting them to ion beam analysis (IBA) using the PIXE technique.

Conversion of Concentration values from Parts per million (ppm) to Percentage %

The PIXE concentration values of the elements generated in parts per million (ppm) were converted to percentage (%) concentration as follows:

1 ppm = $\frac{1}{1,000,000}$

In % = $\frac{1}{1,000,000} \times 100 = \frac{1}{10,000}$

To convert Xppm to X% = $\frac{Xppm}{10,000}$

RESULTS AND DISCUSSION

The results of the elemental analysis of rice husk sample using the PIXE spectrometric technique revealed the presence of a total of thirteen (13) elements as shown in Table1. The PIXE spectrum for the virgin rice husks is shown in. Fig.1. The concentration values in the PIXE spectrum are in parts per million (ppm) due to the high sensitivity of PIXE, but were converted to percentage (%) concentration as presented in Table 1. The predominant element was found to be Si in the form of silica (SiO_2 with a concentration of ~ 26% which is close to some literature values [20]. This high concentration of silica in rice husks is what makes it a bio-resource of interest to researchers. Ti and Zn were found in trace quantities, Al, Fe, Ca, Mg, Na, K, S, Cl, Mn were present in minute quantities while P was present in a small amount relatively. This concentration trend is in conformity with that obtained for rice husk ash (RHA).

The total concentration value of the thirteen elements is 27.158% out of which silica makes up 26 % and the twelve other elements make up only 1.3354%, which is considerably low and of no commercial value like silica. This shows that silica constitutes 95% of the total elements found present in the rice husk sample analysed. Due to their extremely low levels, the other twelve elements are usually regarded as impurities in rice husk ash when the husks are burnt [27]. Since the concentration of the elements is 27.158%, it implies that the balance of 72.842% is made up of the lignocellulosic components of rice husks, with water and extractives. These values are in conformity with values reported in literature [18, 19].

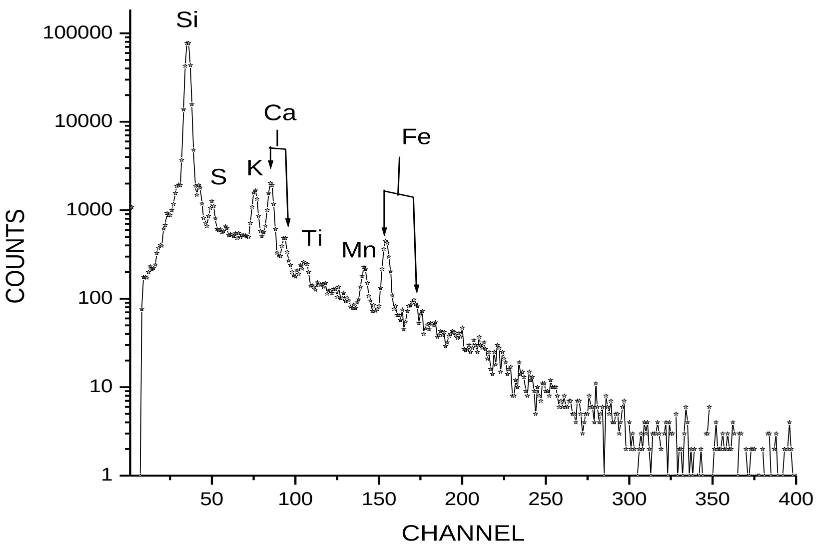

Fig.1 PIXE Spectrum of Rice Husk

Table 1. Elemental Components of Rice Husk using PIXE technique

Element	**Concentration (%)**	**Standard Error (%)**
Si as SiO_2	25.82	0.024
Al	0.017	0.001
Fe	0.039	0.001
Ca	0.088	0.002
Mg	0.135	0.020
Na	0.031	0.010
K	0.099	0.003
P	0.666	0.023
S	0.217	0.009
Cl	0.026	0.005
Ti	0.006	0.001
Mn	0.012	0.001
Zn	0.001	0.000
	27.158	

The concentration value obtained for silicon present in the form of silica (ash) is appreciably higher than some literature values of 15-20% [16, 18, 19] but close to some (22-29%) [21].

Some of these thirteen elements detected in rice husks using the PIXE technique have been reported by other X-ray emission analytical techniques such as X-ray fluorescence (XRF). The elements reported are Fe, Ca, K, Cl, Mn and Zn [27]. The elements not detected by PIXE but have been reported to be present using the XRF technique are Cr, Ni, Cu, Sr, Br, I, and As [27] while those detected by PIXE but not found using XRF are Al, Mg, Na, P,S, and Ti. This variation in the elemental components of rice husks can be attributed to a number of factors such as rice variety, soil chemistry, use and type of fertilizer, climatic conditions etc as earlier enumerated [32-35]. The sensitivity and limitations of the analytical technique employed, can also affect the elements detectable, for instance, XRF, a commonly used X-ray emission analytical technique has some inherent design deficiencies which have reduced its sensitivity to some elements [36].

Expectedly, the elements found in rice husks were also detected in rice husk ash (except for Rb) using the PIXE technique [28]. This therefore substantiates and also confirms the presence of these elements in rice husks. The concentration values of the thirteen elements were lower in rice husks than in rice husk ash. This observation can be ascribed to the presence of water and lignocellulosics in rice husks which give a larger weight and volume of material than in the ash. When these are removed during combustion, the reduction in weight and volume of the rice husk ash residue will give rise to higher concentration values of these same elements in the ash. For instance, Fe, Ca and Mg have concentration values (in %) of 0.039, 0.088 and 0.135 respectively in rice husks, but 0.116, 0.136 and 0.543, respectively in rice husk ash [28], showing a considerable increase in value due to the smaller volume of rice husk ash.

This explanation is also applicable to the concentration of silica in both rice husks and rice husk ash, which values are 25.82% and 74-81% [28], respectively. The level of silica is again higher in the ash than in the husk because when rice husk is burnt, the water, lignocellulosics and volatiles in the husk escape leaving a smaller weight and volume of residue, which has the same silica content (and small amounts of metallic oxides). This is attributable to the fact that silica does not decompose readily during burning due to its high melting point of 1440^0C [33], thus it is the major component of the residue from the combustion process, which is referred to as 'ash' while the other metallic oxides are often referred to as impurities due to their small concentrations[27]. In furtherance of this phenomenon, it has been established that virgin rice husks contain about 15-20% of ash which is largely silica [16, 18-19]. Research findings [37] have shown that when rice husk is incinerated, the ash yield is 19-24%. Thus, 15-20% of silica in 19-24% of ash will give higher silica concentration values in rice husk ash of 79-83%, theoretically. This is close to actual values of silica found to be present in rice husk ash samples which were in the range of 68-91% depending on combustion temperature and duration [38].

CONCLUSION

A total of thirteen (13) elements were detected in virgin rice husks by the PIXE analytical technique with silicon (present in the form of silica) as the predominant element having the highest concentration value of ~26%. The other twelve elements made up 1.3354% out of a total concentration of 27.158 %. This evidently shows that silica constituted about 95% of the elements found present in the rice husk sample analysed while the twelve other elements made up only 5%. Some of the twelve other elements were in minute quantities while some were in trace quantities. The presence of these same elements (except Rb) in rice husk ash as earlier reported substantiates their presence in rice husks. However, the concentration values of the elements in rice husks were found to be lower than those of rice husk ash due to the larger volume of material. The presence of six elements- Fe, Ca, K, Cl Mn and Zn in rice husks has been reported using the XRF technique.

ACKNOWLEDGEMENT

The author is immensely grateful to Prof. E.I Obiajunwa of the Centre for Energy Research and Development (CERD), Obafemi Awolowo University (OAU), Ile-Ife, Nigeria for carrying out the analysis of rice husk using PIXE spectrometric technique.

REFERENCES

[1] Patel, S.A., Onkarappa, R and Shobha, K.S., 2007, "Fungal Pretreatment Studies on Rice Husk and Bagasse for Ethanol Production", Electronic Journal of Environmental, Agricultural and Food Chemistry (EJEAFChe), (6) 4. pp.1921-1926.

[2] Chiang, K., Chou P., Hua, C., Chien, K and Cheeseman, C., 2009. "Lightweight Bricks Manufacture from Water Treatment Sludge and Rice Husks", Journal of Hazardous Materials, vol. 171, issues 1-3, pp. 76-82.

[3] Osarenmwinda, J.O and Nwachukwu, J.C., 2007, "Effect of Particle Size on Some Properties of Rice Husk Particleboard", Advanced Materials Research, vols.18-19, 43-48

[4] Hosseina, A., Hashtroudi, M.S. & Banifatemi, M., 2007 "The use of rice husks to remove wastewater surfactants,Water and Wastewaters" Asia, July/August 2007 http://www.waterwastewaterasia.com/www_archive jul/Aug 07/52t55.pdf.

[5] http://en.wikipedia.org/wiki/rice_husk

[6] http://en.wikipedia.org/wiki/heating_valu

[7] http://www.thejakartapost.com/news/2009/01/28/rice-husk-waste-turned-cheap-energy-cooking.htm

[8] Igwebike-Ossi, C.D., 2012, "Rice Husk Ash as New Extender in Textured Paint" J. of Chem Soc of Nig, vol. 37, no.1 pp. 72-75

[9] Igwebike-Ossi, C.D., 2012," Rice Husk Ash as New Flatting Extender in Red Oxide Primer" J. of Chem Soc of Nig, vol. 37, no.2, pp. 59-64

[10] Igwebike-Ossi, C.D., 2014, "Rice Husk Ash as Flatting Extender in Cellulose Matt Paint" American Journal of Applied Chemistry, vol.2, no.6, pp.122-127

[11] Ohoke, F.O and Igwebike-Ossi, C.D., 2015. "Formulation and Performance Evaluation of Wood Adhesives Produced with Rice Husk Ash as New Filler",

American Journal of Applied Chemistry*,*vol. 3, no. 2, pp.33-39.

[12] Farooq, M. A. and Dietz, K.J., 2015, "Silicon as versatile Player in Plant and Human Biology: Overlooked and poorly understood" Front Plant Sci, 6, p.994

[13] Hodson, M .J., White, P.J., Mead, A., Broadly, M.R, 2005," Phylogenetic Variation in the Silicon Composition of plants, Annal. Bot, 96, pp. 1027-1046

[14] Juliano, B.O., 1985, "Rice Husk and Rice straw", St. Paul, MN(USA) – American Association of Cereal Chemists pp.689 – 695.

[15] Bharadwaj, A., Wang, Y., Sridhar, S., and Arunachobam, 2004, "Pyrolysis of Rice Husk" Current Science, vol. 87, no. 7, pp.981-986 http://www.ias.ac.in/currsci/oct10.2004/98/pdf

[16] Muntohar, A.S., 2002, "Utilization of uncontrolled Burnt Rice Husk Ash in Soil improvement", Dimenia Teknik Sipil vol.4 no. 2 pp. 100 – 105

[17] Govindaro, V.M.H., 1980, "Utilization of Rice Husk – A Preliminary Analysis ", J. Sci. Ind. Research, 39, pp. 495-515.

[18] Daifullah, A. A. M., Girgis, B.S., and Gad, H.M.H., 2003, "Utilization of Agro-residues (Rice Husk) in Small Wastewater Treatment Plans", Material Letters, 57, pp. 1723-1731.

[19] Arnesto, L., Bahillo, A., Veijoren K., Cabanillas A. and Otero, J., 2002, "Combination Behaviour of Rice Husk in a Bubbling Bed", Biomass and Bioenergy, 23, pp. 171-179

[20] Balakrishnan, S. 2006, "Rice Husk Ash Silica as a Support Material for Iron and Ruthenium-Based Heterogeneous Catalyst". M.Sc Thesis,School of Chemical Sciences, Universiti Sains Malaysia.

[21] Maeda, N., Wada, I., Kawakami, M., Ueda, T and Pushpalal, G.K.D., 2001, "Development of a New Furnace for the production of Rice Husk Ash" The seventh CANMET/ACI International Conference on Flyash, Silica fume, Slag and Natural Pozzolans in Concrete, Vol. 2, Chennai, July, 22-27 p.835.

[22] Subbukrishna, D.N., Suresh, K.C., Paul, P.J, Dassapa, S and Rajan, N.K..S., 2007, "Precipitated silica fromRice Husk Ash by IPSIT process" 15th European Biomas Conference and Exhibition, 7-11 May, Berlin,Germany. http://cgpl.iisc.ernet.in/site/portals/0/Technologies/precipited silica.pdf. http://www.ehow.com/about_4600805_what-silicon-dioxide.html

[23] Chockalingam, E., Sivopriya, K., Subramanian S. and Chandrasekaran 2005, "Rice Husk Filtrate as a Nutrient medium for the growth of Desulfotomaculum nigrificans Characterization and Sulfate Reduction Studies" .Bioresour Technol. 96(17): 1880-1

[24] Janvijitsakul, K. and Kuprianov ,V.I., 2006, "Polycyclic Aromatic Hydrocarbons in Coarse Fly Ash Particles Emitted from Fluidized Bed Combustion of Thai Rice Husk", In Proceedings of the 2nd Joint International Conference on Sustainable Energy and Environment (SEE), Thailand, 21-23, November, 2006, pp. 378-383

25] Kwong, P.C.W., Wang, J.H., Chao, C., Cheung, C.W and Kendal,l G., 2004, "Effect of Co-Combustion of Coal and Rice Husk on Combustion Performance and Pollutant Emission" The seventh Asia-pacific International Symposium on Combustion and Energy Utilization, Dec., 15-17, 2004, Hong Kong, SAR

[26]. Habeeb, G.A and Fayyadh, M.M., 2009, "Rice Husk Ash Concrete: the effect of RHA Average particle size on mechanical properties and drying shrinkage," Australian Journal of Basic and Applied Sciences*,* 3, no.3, pp. 1616-1622.

[27] Omatola, K.M and. Onojah, A.D., 2009, "Elemental Analysis of Rice Husk Ash using X-ray Fluorescence Technique",International Journal of Physical Sciences 4 (4) pp. 189-193 http://www.academicjournals.org/IJPS.

[28] Igwebike-Ossi, C.D**.,** 2016 "Elemental Analysis of Rice husk ash using Proton-induced X-ray Emission (PIXE) Spectrometry", International Journal of Applied Chemistry, vol. 12, No.3 pp.233-242

[29] Oyawale, O.O., 2012, "Characterization of Rice Husk via Atomic Absorption Spectrometry", International Journal of Science and Technology", 2**,** no 4 pp. 210 – 215.

[30] Johanssen, A.E Campbell, J.L and Malmqvist, K.G., 1995, "Particle-Induced X-ray Emission Spectrometry (PIXE), Chemical Analysis – A series of Monographs on Analytical Chemistry and its Application" , John Wiley and Son Inc. New York , pp. 1- 17.

[31] http://www.elementalanalysis. com/service pixe.com

[32] Chandrasekar, S Satyanarayana and Raghavan, P.N., 2003, "Processing, properties and Applications of Reactive Silica from Rice Husk – An Overview" Journal of Materials Science, 38,p. 3159.

[33] Rice Husk Ash Market Study Confidential Report, 2003, http:// webarchives.nationalarchives.gov.uk

[34] Mehta, P.K., 1994, "Rice Husk Ash- A unique Supplementary Cementing Material," Advances in Concrete Technology, MSL Report, **94**, CANMET, pp. 419-444.

[35] Real, C., 1996, "Determination of Silica from rice husk ash," J.Amer. Cerem

Soc.79, 18: pp. 2012-2016.

[36] Jenkins, R., 1999, "X- ray Fluorescence Spectrometry," Wiley Interscience, New York, pp. 5-7

[37] Igwebike-Ossi, C.D and Ibemesi, J.A., 2010, "Effects of Combustion Temperature and Time on Ash Yields of Rice Husks", Journal of Chemical Society of Nigeria, vol. 35 no. 1, pp. 134-137.

[38] Igwebike-Ossi, C.D and Ibemesi, J.A., 2011, "Determination of Silica content of Rice Husk Ash at Various Combustion Temperatures and Time using Particle-induced X-ray Emission Spectrometric Technique", Journal of Chemical Society of Nigeria, vol. 36, no. 1, pp. 42-46