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EXTRACTION AND CHARACTERIZATION OF SOLAR-GRADE BIOSILICA FROM RICE HUSK

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ABSTRACT

The paper presents the extraction and characterization of biosilica from rice husk with the aim of investigating its possible use as raw material for the production of solar cells. Rice husk from three different rice varieties (ITA 150, NERICA II and ITA 157) that are mostly grown and available in Katsina, Kaduna, and Kano states, of Nigeria, were obtained. The rice husks samples were cleaned and combusted for 1hour at temperatures of 500^oC to 1000^oC and then acid-leached with HCl to remove some impurities to obtain rice husk ash (RHA). Characterization of the extracted RHA samples was done using Energy Dispersive X-ray (EDX) spectrometry and Scanning Electron Microscopy (SEM). The results show that the maximum silicon oxide (Biosilica) contents in ITA 150, NERICA II and ITA 157 were 14.25 wt%, 14.31wt% and 25.19t% respectively, corresponding to combustion temperatures of 610^oC, 715^oC, and 638^oC. From a given mass of rice husk (30g), the extracted biosilica from the respective rice varieties were 10.91g, 6.58g, and 16.64g respectively. The SEM micrographs of the RHA obtained at combustion temperatures of 610^oC, 715^oC, and 638^oC suggests the structure to be amorphous, while the structure of the ash obtained at combustion temperatures above 800-1000 ^oC suggests a crystalline structure.

Keywords: *Amorphous; Biosilica; Crystalline; Rice Husk Ash (RHA); Solar Cell.*

INTRODUCTION

Rice husk is an irregular boat-like particle with dimensions about 8–10 mm in length, 2–3 mm in width and 0.2 mm in thickness. It is very light, with packing density of 122 kg/m^3. Rice husk is also characterized by high volatile matter content, a nearly uniform size and high ash melting points [1]. In the composition of rice husk on dry basis, carbon content has highest percentage, followed by oxygen. This means that it supports combustion and burn easily to obtain ash. Rice husk is an agricultural by-product whose major constituents are organic materials and hydrated silicon. Because the silicon atoms in the rice husk have been naturally and uniformly dispersed by molecular units, silica powder with very fine particle size, with very high purity and surface area, can be obtained under controlled conditions. The chemical properties of ash arising from rice husks are thought to vary from region to region. The differences have been attributed to the conditions under which the paddy is grown, such as climate, soil, and use of fertilizers [2]. The organic materials in rice husk consist of celluloses (55–60%, including cellulose and hemicellulose) and lignin (22%). Approximately one-fifth of the ash could be obtained on burning rice husk in air [3]. The desirable physico-chemical and mechanical properties of amorphous silica, notably their high reactivity, excellent binding properties, relatively high purity and excellent mechanical strength make this material useful in a wide range of technologies. Although hosts of synthetic silica are produced commercially, the ones produced from plant origins such as rice husks have been noted to have some significant advantages over those from mineral and synthetic origins [4]. In particular, the processing steps are relatively simple and require no elaborate infrastructure or consumption of costly reagents as in the case of the synthetic processes. In addition the final silica powder produced from plant sources contains a narrow range of metal oxide impurities which makes them exceptionally desirable in applications where high purity silica at modest cost is a necessary prerequisite [4].

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 [5]. RHA has been evaluated as an adsorbent of minor vegetable oil components [6]. Soluble silicates produced from silica are widely used in the glass, ceramics, and cement as a major component and in pharmaceuticals, cosmetics, and detergents industries as a bonding and adhesive agents [7]. Silica also has been used as a major precursor for a variety of inorganic and organometallic materials which have applications in synthetics chemistry as catalysts, and in thin films or coatings for electronic and optical materials [8].

Rice is produced in at least 35 of Nigeria's 37 States, covering three major ecological zones: rain-fed upland, rain-fed lowland and irrigated. Production in the rain-fed upland system is largely subsistence-based, while production in the rain-fed lowland and irrigated systems is commercially oriented [9]. Although the potential global estimate of Rice Husk Ash (RHA) production is 21,000,000 tones, 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 going into landfill [2]. As reported in the literature, the purity level of solar-grade silicon is considerably less than that of semiconductor-grade silicon. Therefore, the cost of manufacturing solar cells can be considerably reduced by investigating new and inexpensive source of materials [10] [11]. Worldwide efforts are being made to develop a low cost, high volume and commercially feasible process for production of high-purity silicon for use in the production of solar cells. The main objective of this paper is to investigate the suitability of biosilica (silica from rice husk) for possible applications in solar cell technology. Rice husk is a by-product of rice milling industries. Rice is grown on every continent (except Antarctica) and covers 1% of the earth's surface. Rice production in Nigeria has been estimated to about 500,000 tones annually. Rice husk makes up 40% of unmilled rice grain, and Nigeria has the potential to produce about 200,000 tones of rice husks annually [12]. During growth, rice plants absorb silica from the soil and accumulate it into their structures [13]. This valuable resource (silica) could be extracted from rice husk and then be processed to obtain solar grade amorphous silicon – a raw material for the production of a-Si solar cell.

MATERIALS AND METHODS

Extraction of Rice Husk Ash from Rice Husk

Rice husk ash was extracted according to the method of Proctor and Palaniappan [14], John *et al.* [15] and Singh *et al.* [16]. Rice husk of three different rice varieties (ITA 150: sample A, NERICA II: sample B, and ITA 157: sample C) that are prevalent in Katsina, Kaduna, and Kano states of Nigeria [9] were obtained, cleaned thoroughly with distilled water to remove adhering soil and dust and then dried in an oven at 105^oC for 4hours. 30g of each sample of the rice husk was poured into crucibles and placed in an electric furnace (Gallenkamp, Muffle Furnace, size 2) for combustion at a temperature of 500^oC for 1hour. The ashes obtained were allowed to cool in the furnace to room temperature. The ashes were acid leached by heating the mixture of dilute HCl and RHA on a hot plate at 100^oC for 1hr to remove soluble impurities and then washed with distilled water, dried and re-weighed. The above process was repeated for the temperatures of the electric furnace kept at 600^oC, 700^oC, 800^oC, 900^oC, and 1000^oC.

Energy Dispersive X-Ray (EDX) Spectrometry

Mini Pal x-ray spectrometer was used to determine the elemental composition of RHA samples. The system is controlled by a PC running the dedicated Mini pal analytical software. The Mini pal 4 version in use is PW 4030 X-ray spectrometer, which is an energy dispersive microprocessor controlled analytical instrument designed for the detection and measurement of elements in a sample (solid, powder or liquid). The samples were weighed and grounded in a mortar and a binder (PVC dissolved in Toluene) was added. The samples were carefully mixed separately and pressed in a hydraulic press into pellets. The pellets were loaded, one after the other, into the sample chamber of the spectrometer with its voltage and current set at 30kV and 1mA to produce the x-ray to excite the sample for 10 minutes. The spectrum from the sample was then analyzed to determine the concentration of the elements in the sample.

Scanning Electron Microscopy (SEM)

Sample specimen was taken and coated with gold in a gold sputter coater for 70 seconds at 15mA current output. The scanning election microscope was set at 20kV and working distance of 14mm. Then the selected area of interest was focused and micrograph was taken. The procedure described above was carried out for the remaining samples and results presented in Figures 1 to 3.

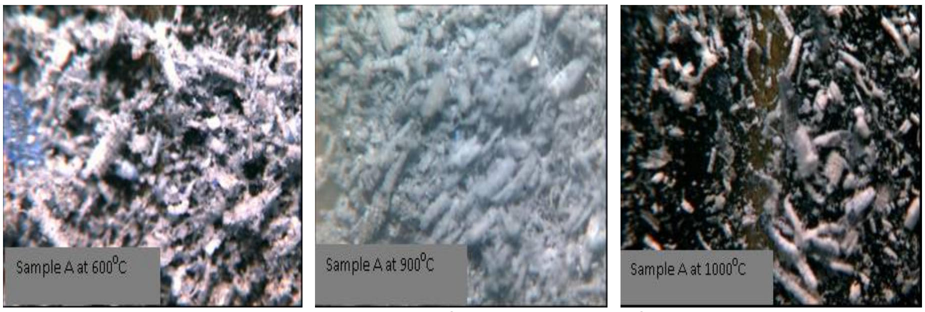

Fig. 1: SEM Micrograph of ITA 150, Magnification x20

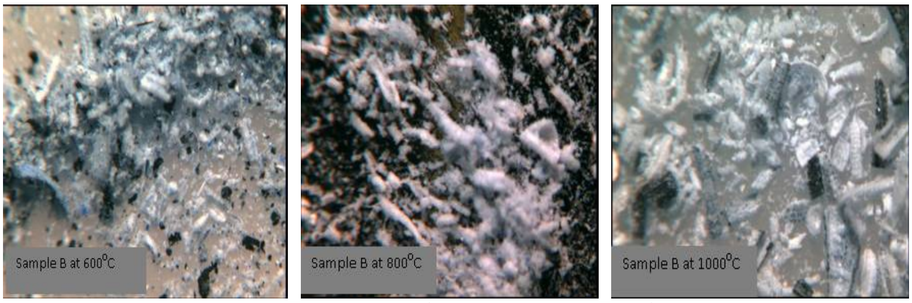

Fig. 2: SEM Micrograph of NERICA II, Magnification x20

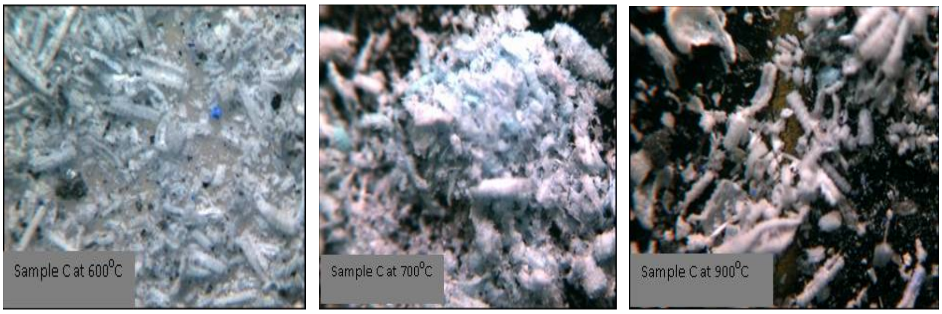

Fig. 3: SEM Micrograph of ITA 157, Magnification

RESULTS AND DISCUSSION

The product of the combustion of the rice husk is the rice husk ash. The RHA was acid leached with HCl to remove some impurities. It was observed that the mass of the rice husk ash from the three different varieties of rice samples used decrease with the increase in the combustion temperatures (Table 1).

Table 1: Mass of RHA after acid leaching with HCl

	Mass of Rice	Mass of Rice Husk Ash, (g)

Rice Husk Varieties	Husk Before Combustion, (g)	500^oC	600^oC	700^oC	800^oC	900^oC	1000^oC
NARICA II(Sample B)	30	14.4	12.04	9.39	7.04	6.05	5.94
ITA 150 (Sample A)	30	11.69	9.11	6.82	5.35	4.94	4.47
ITA 157 (Sample C)	30	16.86	16.79	15.81	13.85	10.90	10.14

The rice husk ash samples were pelletized and loaded in the spectrometer's sample chamber for X-ray excitation. The spectrum from the sample was analyzed and the chemical compositions of the RHA are shown in the Tables 2-4. It was observed that the biosilica (silicon oxide) content of the three different rice husk ash samples combusted had a non-linear relationship. Silicon oxide content initially increased with increase in the combustion temperature to a maximum at a temperature of around 600°C and later decreased with increase in combustion temperature.

Table 2: Chemical composition of RHA of ITA 150 (Wt %)

Oxide Element	500^oC	600^oC	700^oC	800^oC	900^oC	1000^oC
SiO_2	55.90	94.96	77.20	72.70	71.00	71.60
P_20_5	0.100	1.300	0.810	0.400	1.500	1.200
SO_3	1.100	0.170	0.810	0.200	-	-
Cl	0.130	0.143	1.010	0.160	0.220	-
CaO	0.491	0.228	0.441	1.120	0.350	0.391
Fe_2O_3	0.619	0.533	0.629	0.420	0.646	0.391
Rb_2O	34.00	-	17.00	23.00	24.00	24.00
CdO	5.200	-	-	-	-	-
Al_2O_3	-	1.700	0.400	0.200	-	-
K_2O	-	0.444	1.010	0.665	0.955	1.410

Table 3: Chemical composition of RHA of NERICA II (Wt %)

Oxide Element	500^oC	600^oC	700^oC	800^oC	900^oC	1000^oC
SiO_2	71.80	88.25	94.50	91.90	92.24	93.97
P_20_5	0.520	6.230	1.200	3.200	2.300	1.200
SO_3	12.30	0.091	-	-	-	0.094
Cl	0.627	0.240	0.150	0.737	0.392	0.815
CaO	0.442	0.973	0.562	0.351	0.628	0.421
TiO_2	0.130	0.074	0.053	0.110	0.140	0.091
MnO	0.052	0.260	0.061	0.079	0.097	0.069
Fe_2O_3	0.448	0.790	0.351	0.612	0.748	0.376
Rb_2O	13.00	-	-	-	-	-
BaO	0.150	0.100	0.140	0.130	0.140	0.150
Al_2O_3	0.300	1.800	1.800	1.700	1.800	1.600
K_2O	0.627	0.934	0.790	0.745	0.861	0.809

Table 4: Chemical composition of RHA of ITA 157 (Wt %)

Oxide	500^oC	600^oC	700^oC	800^oC	900^oC	1000^oC

Element						
SiO_2	65.40	84.56	91.38	60.10	72.60	71.20
P_20_5	-	9.510	1.400	0.680	0.960	1.000
SO_3	4.110	-	0.120	-	-	-
Cl	-	0.338	1.680	0.518	0.329	0.300
CaO	0.310	1.100	0.469	0.320	0.300	0.433
Fe_2O_3	0.299	0.604	1.390	0.441	1.140	0.674
Rb_2O	24.00	-	-	32.00	22.00	24.00
CdO	3.600	-	-	4.900	-	-
BaO	0.190	0.110	0.120	0.200	0.190	0.190
Al_2O_3	-	1.400	1.700	-	0.100	-
K_2O	-	1.360	1.030	-	0.738	0.880

Sample of the rice husk ash was coated with gold in a gold sputter for 70 seconds at 15mA of current output. Micrographs of selected area of interest were taken and the SEM images are presented in Figures 1-3. The masses of the extracted rice husk ash of the three different rice varieties samples A, B, and C at various combustion temperatures were shown in the Table 1. It was observed that from 30g of rice husk drawn from samples A, B, and C at the combustion temperature of 500^oC, the masses of RHA were 11.4g, 11.69g, and 16.86g while, at combustion temperature of 1000^oC the masses were respectively 5.9g, 4.4g, and 10.1g . However, the mass of the rice husk ash of the samples decrease with increase in combustion temperature. Sample C has the highest mass of RHA of 10.1g at the combustion temperature of 1000^oC. This variation may be attributed to the peculiarities in paddy rice variety as suggested by Real [17].

Oxides of thirty elements were detected in all by the EDX method analysis with varying concentrations. The silicon oxide content of the RHA from samples A, B, and C were 96.25 wt%, 94.95wt%, and 91.83wt% and their respective combustion temperatures were 610^oC, 715^oC, and 638^oC. Sample A has highest percentage purity level of silica followed by sample B and then sample C. These variations again could be due to the difference in rice husk variety, soil chemistry of the locations of collection of the samples and type of chemical fertilizers used as suggested by Mehta [18]. The extracted mass of biosilica from samples A, B, and C were deduced as 10.91g, 6.58g, and 16.64g respectively.

The morphology of biosilica extracted from rice husk samples are presented in Figures 1-3 with the magnification of 20 times. The structures of the extracted biosilica samples corresponding to combustion temperatures of 610^oC, 715^oC, and 638^oC show no evidence of ordered arrangement of crystals - this means the biosislica obtained is amorphous.

However, the structure of the biosilica samples obtained at combustion temperatures higher than 800^oC is having an ordered arrangement of atoms as observed by Joseph *et al.* [19] – this means the material is crystalline biosilica. The change of the amorphous ash to crystalline ash occurs at a temperature between 800^oC and 900^oC as observed by Sugita [20]. Close examination of the silica images show that the particles of the silica obtained at combustion temperatures 900–1000°C have porous structure with homogeneous particle distribution as described by Yalcin and Sevic [21].

CONCLUSION

The silica potential of rice husk of three different rice varieties (ITA 150, NERICA II, and ITA 157) that are widely grown and available in Katsina, Kaduna, and Kano states were investigated. Biosilica was extracted from rice husk through combustion in a Gallenkamp, Muffle Furnace and subsequent leaching with concentrated hydrochloric (HCl) acid. Characterization of the extracted silica from the rice husk samples by Energy Dispersive X-ray (EDX), and Scanning Electron Microscopy (SEM) revealed that the maximum silicon oxide content of ITA 150, NERICA II, and ITA 157 were 14.25 wt%, 14.31wt% and 25.19wt% respectively obtained at corresponding combustion temperatures of 610^oC, 715^oC, and 638^oC. ITA 150 has highest percentage purity level of silica followed by NERICA II and then ITA 157 with low impurity concentration level. The estimated masses of biosilica from the samples at were deduced to 10.91g, 6.58g, and 16.64g respectively from 30g of rice husk. The SEM micrographs of the RHA obtained at combustion temperatures of 610^oC, 715^oC, and 638^oC suggests the structure to be amorphous, while the structure of the ash obtained at combustion temperatures above 800^oC suggests a crystalline structure as described by Joseph *et al.* [19]. The change of the amorphous structure to crystalline occurred between 800^oC and 900^oC as explained by Sugita [20]. The RHA can further be processed to obtain pure (100%) amorphous or crystalline silicon depending on the combustion temperature. Rice husk which is an agricultural waste can be used as a source of raw material for the production of either amorphous or crystalline silicon, which could subsequently be used for the production of solar cells.

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REFERENCES

[1] Chandrasekhar, S.; Satyanarayana, K.G.; Pramada, P.N.; Raghavan, P.; and Gupta, T.N. (2003). Processing, Properties and Applications of Reactive Silica from Rice Husk - an overview. *Journal of Materials Science*. vol. 38, pp. 3159-3168.

[3] James, J. and Rao, M.S. (1986). Silica from Rice Husk through Thermal Decomposition. *Thermochimica Acta*, vol. 97, pp. 329-336, 1986.

[2] Velupillai L,; Mahin D.B,; Warshaw J.W,; and Wailes E.J (1997). A study of the Market for Rice Husk –to Energy Systems and Equipment. *Louisiana State University Agricultural Center USA.*

[5] Owens, P., (1999). Pulverized Fuel Ash Part 1: Origin and Properties, *Current Practice sheet* No. 116. Concrete Vol. April. p. 27.

[4] Zemnukhova, L.; Egorov, A.; Fedorishcheva, G.; Barinov, N.; Sokolânitskaya, T.; and Botsul, A. (2006). Properties of Amorphous Silica Produced from Rice and Oat Processing Waste. *Inorganic Materials*, vol. 42, pp. 24-29.

[6] Proctor, A.; Clark, P.K.; and Parker, C. A., (1995). Rice Hull Ash Adsorbent Performance Under Commercial Soy Oil Bleaching Conditions. *Journal of America Oil Chemical Society*, vol. 72, pp.459-462.

[7] Anon, (1999). Soluble Silicates and their Applications. *Crossfield Publication, Crossfield, Warrington, UK,* Issue No. 2

[8] Lender, P. W,; and Ruiter, R. (1990). Novel Inorganic Materials and Heterogeneous Catalysis: Preparation and Properties of High Surface Area Silicon Carbide and Silicon Oxynitrides. *In Sheats, J.E.*

[9] KTARDA (2010). Katsina State Agricultural and Rural Development Authority, *Funtua Zone Office, Funtua.*

[10] Bathey, B.R. and Cretella, M.C., (1982). Review of Solar-Grade Silicon. *Journal of Materials Science.* vol. 17, pp. 3077-3096.

[11] Bose, D. N.; Govindacharyulu P. A.; and Banerjee, H. D. (1982). Solar Energy Matter. *Journal of Materials Science*, vol. 17, pp. 3077-3096.

[12] Aderolu, A.; and Oyedokun G., (2009). Comparative Utilization of Biodegraded and Undegraded Rice Husk in Clarias Gariepinus Diet. *African Journal of biotechnology* vol 8, pp. 1358-1362.

[13] Singh, R. and Dhindaw, B.K. (1978). Production of High Purity Silicon for use in Solar Cells. *Proceedings of the International Solar Energy Congress*. pp. 776-781

[14] Proctor, A. and Palaniappan, S. (1990). Adsorption of Soy Oil Free Fatty Acids by Rice Hull Ash. *Journal of America Oil Chemical Society*. Vol 67, 15-17.

[15] John, A.; Alexanda, S.; and Larry, A. (2001). Approaching a Universal Sample Preparation Method for XRF Analysis of Powder Materials. *Journal of Materials Science*. 44, 368-370.

[16] Singh, D.; Kumar, R.; Kumar, A.; and Rai, K. N., (2008). Synthesis and Characterization of Rice Husk Silica, Silica-carbon Composite and H3PO4 Activated Silica. *Cerâmica*, vol. 54, pp. 203-212.

[17] Real, C.; Alteala, M. D.; and Criado, J. M., (1996). Preparation of Silica from Rice Husks. *Journal of the American Ceramic Society*. 79, 2012-2016.

[18] Mehta, P.K., (1994). Rice Husk Ash – A Unique Supplementary Cementing Material In Advances in Concrete Technology. *CANMET*. pp. 419 – 444.

[19] Joseph, S.; Baweja, D.; Crookham, G.D.; and Cook, D.J., (1989). Production and Utilization of Rice Husk Ash Preliminary Investigations. *Third CANMET/ACI International conference on fly ash, silica fume, slag and natural pozzolans*. pp. 861-878.

[20] Sugita, S. (1993). On the Economical Production of Large Quantities of Highly Reactive Rice Husk Ash. *International Symposium on Innovative World of Concrete* (ICI – IWC – 93). 2: 3–71.

[21] Yalcin, N.; and Sevic, V., (2001). Study on Silica Obtained from Rice Husk, Ceramics *international.*, Vol. 27, pp 219-224.