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Original Research Paper

Physical, chemical and electric characterization of thermally treated rice husk ash and its potential application as ceramic raw material

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ABSTRACT

Rice husk ash (RHA) is composed essentially by carbon and high levels of silica that justify the economically viable use of RHA in production of ceramic materials. Therefore, this study presents the physical, chemical, and electric characterization of two RHAs submitted to thermal treatment at different temperatures. Grain size, specific weight, specific surface area, total carbon analysis as well as X-ray fluorescence spectrometry, scanning electron microscopy, X-ray diffraction, and complex impedance spectroscopy were carried out. The results indicate that the thermal treatments afforded to produce high-silica RHA with cristobalite and tridymite crystalline phases that indicate the potential of RHA to be used as raw material to obtain advanced silica-based ceramic products. RHA particle size increased with treatment temperature, followed by a slight increase in specific weight and a drastic drop in surface area. Electrical characterization showed that silica particles are closely packed to a carbon film.

1. Introduction

In the effort to discover new, low-cost materials and technologies and to minimize environmental problems, considerable research on renewable raw materials, byproducts, and industrial waste is carried out. As a rule, silica has several applications in a variety of areas. Silica is used as raw material in the production of electronics, ceramics, polymers, medical drugs, adhesives, as well as in the processing of vegetable oil and as packing material of chromatography columns [1,2]. However, the production of silica from ores is based on high-temperature, energy-intensive physical and chemical operations that require large amounts of acids, generating considerable volumes of chemical waste [3].

On the other hand, with considerable silica contents, rice husk ash (RHA) is byproduct widely available in rice producing nations, requiring proper methods of utilization or disposal [4,5]. Though rice husk is a low-cost raw material, reuse at source is made difficult due to undesirable characteristics such as abrasivity, poor nutritional value and digestibility, high resistance to decomposition, and impracticable storage requirements. With high heat value, rice husk is mainly used in energy generation by combustion. Recycling and composting stand as interesting disposal alternatives for rice husk; however, the current global energy scenario and the quest for renewable energy sources point to combustion for energy production as the most environmentally friendly and economically suitable solution for rice husk [6].

'Rice husk ash' represents all varieties of ash generated in rice husk combustion. However, this material's properties vary considerably with combustion settings [7]. Besides being light, bulky, and highly porous [8], composition of RHA includes silica (SiO_2), carbon (C), potassium oxide (K_2O), phosphoric oxide (P_2O_5), calcium oxide (CaO), and smaller amounts of magnesium (Mg), iron (Fe), and sodium (Na) [9].

With several applications in several industries, RHA has been used as pozzolanic material in construction [10] and adsorbent material [11]. In addition, RHA is also used in the production of ceramics, as raw material in the manufacture of glasses and refractory materials [12], as replacement of quartz to obtain whiteware [13], and as source of silica to produce zeolites [14].

The high silica levels make RHA an economically attractive raw material in the production of pure silica, advanced ceramic materials like silicon carbide (SiC) and nitride (Si_3N_4), and even high-

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purity metallic silicon [4,15,16]. In particular, RHA is a low-cost source of silica in the production of SiC and Si_3N_4. In particular, SiC is used to improve surface hardness of cutting and machining tools, though more general applications include the production of wear-resistant devices used in armoring processes [17]. With interesting semiconductor properties such as non-linear resistivity, SiC is a component of protective devices in electrical grids. In turn, Si_3N_4 exhibits the best properties, being used in the manufacturing of engines. High-purity silica is used to produce SiC, silicon tetrachloride ($SiCl_4$), Si_3N_4, and silicon itself [18]. When RHA is used as raw material, SiC may be obtained if temperatures fall below the usual range of 1200–1550 °C, due to the large surface area of RHA particles and improved contact between amorphous silica and carbon atoms. As a result, the SiC particles produced do not agglomerate [15,19].

As in the production of SiC, RHA has been used in the manufacturing of high-purity Si_3N_4 for over 30 years. The main reason is that other methods normally produce the compound accompanied by SiC, due to the presence of contaminants that affect yield and concentration of Si_3N_4. In addition, if the carbon-to-silicon ratio is higher than the stoichiometric amount required for the nitridation reaction, SiC will also be produced. Therefore, the removal of impurities prior to reaction is one of the obstacles faced in the production of Si_3N_4 at industrial scale [18]. Another relevant factor is that most studies published to date have looked into the use of rice husk as a source of silica. The few papers that have investigated RHA used an ash produced under controlled laboratory conditions. Yet, from the industrial standpoint such an experimental model does not exactly reflect the properties of RHA as produced today, that is, by large-scale combustion of rice husk as biomass for energy generation.

In this context, the present study exhibits the physical, chemical, and electrical characterization of residual RHAs from Brazil power plants submitted to thermal treatments at different temperatures and discuss the relationship of these treatments with the electrical and morphological characteristics.

2. Materials and methods

2.1. Materials

The RHAs used in this study were obtained from two companies in the state of Rio Grande do Sul, Brazil. The companies use rice husk as biomass for energy generation. Two RHAs were used, one obtained by combustion in a slanted moving grate reactor (RHA-MG), one in a fluidized bed reactor (RHA-FB). The power generation capacity of these units is 3.8 MW h and 5 MW h, respectively.

RHA-FB is obtained by instantaneous combustion on a sand bed injected with an ascending air flow at approximately 700 °C and milled in the producer company. In turn, RHA-MG is produced at temperatures near 840 °C and provided untreated by the producer company. Therefore, to afford a more reliable comparison with RHA-FB, the RHA-MG as received was sifted through a 1.2-mm mesh, which retained impurities such as unburnt husks, as suggested by Kieling [20]. The passing fraction was milled for 2h20 in an eccentric ball mill (CB2-T).

2.2. Thermal treatment

RHA-FB and RHA-MG were submitted to thermal treatment at different temperatures. Samples were heated in a muffle furnace at 1000 °C, 1200 °C, and 1400 °C for 1 h at a 10 °C min^{-1} heating gradient and left to cool inside the oven down to room temperature.

2.3. Characterization of materials

Thermo gravimetric and differential thermal analysis (TG-DTA) of rice husk ashes was carried out in a simultaneous analyzer (PerkinElmer - STA 8000). Approximately 15 mg of the sample was placed in the microbalance and heated at rate of 5 °C min^{-1} under nitrogen flowing, from room temperature to a final temperature of 1400 °C.

Grain size distribution and particle size was determined wet by laser diffraction in a particle analyzer (S3500, Microtrac). Water was used as solvent, supplemented with one drop of a surfactant, at 25% flowrate and ultrasound time of roughly 30 s.

Specific weight was obtained using a helium gas pycnometer (AccuPyc II 1340, Micrometrics). A 5-g sample was placed in a 10-cm^3 aluminum sample holder previously dried in a stove at 105 °C. Specific surface area of samples was evaluated by nitrogen adsorption in surface area analyzer (TriStar Plus, Micrometrics). Samples were vacuum-degassed at 200 °C for 24 h.

Chemical composition of previously milled samples was analyzed by comparison with a secondary RHA standard using energy-dispersive X-ray spectroscopy (XRF) (EDX 720 HS, Shimadzu). Results were expressed as oxide mass percent and normalized to 100% using carbon percent values. Total carbon (TC) was determined using samples dried by total combustion at 1350 °C by infrared detection in a carbon analyzer (SC-144DR, Leco).

Mineralogical composition was established by X-ray diffraction (XRD) in an X-ray diffractometer (X'Pert, Philips) with Cu-Kα radiation (λ = 1.5418 Å) at 40 kV, 40 mA, and a 5–75° 2θ scanning range. Peaks were identified using the proprietary software (X'Pert High Score 2.0a). Morphology of materials was evaluated using gold-plated samples by high-vacuum scanning electron microscopy (SEM) (Evo MA15, Zeiss) with secondary electron detectors.

Electrical characterization was carried out by complex impedance spectroscopy (CIS) in a potentiostat/galvanostat equipped with a radiofrequency analyzer (Autolab PGSTAT302N, Methrom). Analyses were carried out using 1-g samples compacted in a powder sample holder at room temperature. Spectra were obtained between 1 Hz and 1 MHz and oscillation voltage of 500 mV TOP (AC). The CIS results were analyzed against the data obtained in the chemical characterization and phases observed.

All analyses were carried out using RHAs thermally treated as described in item 2.2 and non-treated samples of RHAs as received, for comparison.

3. Results and discussion

Thermal analysis was carried out to evaluate the weight loss with temperature of the original RHA samples. The TGA/DTA curves of the two raw RHAs used in this study are shown in Fig. 1. Typical little weight loss of water elimination (adsorbed on the particles' surface) can be seen between 30 and 150 °C. Organic matter is degraded between 150 and 600 °C. Carbon particles and carbonates decompose in the 600–800 °C range, emitting CO_2, as it can be seen in the case of RHA-MG. Since this one is richer in carbon content, it lost more weight starting at 150 °C. DTA curve, in the case of RHA-FB, shows an exothermic peak before 200 °C of water elimination and an endothermic peak near 800 °C possibly relative to carbonates decomposition. In the RHA-MG this decomposition possibly occurs before 800 °C probably due to the greater amount of carbon in this RHA. It can be observed that around 1000 °C entire mass loss referring to carbonaceous materials has already occurred. This fact corroborates with the total carbon values obtained, that did not vary with the temperature regimes used (1000 °C, 1200 °C, and 1400 °C) and also the weight loss until

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