The influence of the technological process of rice husk ash synthesis over its structure

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Abstract. In this research, the identification of the influence of several methods of rice husk ashes preparation over their structure was followed, by varying the synthesis parameters, as well as by subsequent application of the grinding process. The obtained rice husk ash samples with high silica composition, were characterized by X-ray diffraction (XRD) to determine the compositional phases and crystalline structure of the samples, by scanning electron microscopy (SEM) to observe the microstructure and the particle sizes, and by laser granulometry to establish the granulometric distribution. Thus, it was possible to conclude that the technological process used for rice husk ash preparation shows influences on the samples microstructure and composite phases, as well as differences in particle sizes by decreasing their values as a result of mechanical process application. Based on these analyses, it was verified which of the obtained rice husk ash samples present a suitable microstructure, in order to capitalize them in environmental applications.

1. Introduction
Taking into account the main problems that population is facing with (the disappearance of natural resources and the production of excess wastes), it is necessary to find solutions for their remediation through the use of wastes produced in the main streams of production. Thus, the aim is to increase the production of products obtained from wastes and secondary raw materials in every branch of industry.

In recent years, the use of waste or by-products from different industries and the agricultural sector has received increasing attention in the scientific, technologic, ecological, economic and social areas [1]. One of the materials of such interest is represented by rice husk, more precisely the rice husk ash obtained through combustion process [2].

Rice husk ash is a waste product generated from power industry. The main compound found in rice husk is amorphous silica which transforms to crystalline silica when it is heated at high temperatures.

Since SiO₂ in industrial rice husk ash waste can exist in both amorphous and crystalline (mostly cristobalite) forms (varying by its heat treatment history), depending on the subsequent applications, it must be considered that the thermal treatment to be applied to rice husks is influenced by its chemical purity and particle size.

According to other research, the ash from the unwashed husk contains about 96% silica and some amount of organics, alkali oxides, and impurities. However, a silica content of up to 99% or even more
may be obtained with an appropriate washing of the husks. K₂O and Na₂O alkanis present in the rice husks, accelerate the transformation of amorphous SiO₂ to cristobalite or tridymite with a decrease in the transformation temperature (from ~1200 °C to 800 °C) [3, 4].

The most important properties (the quality) of rice husk ash such as fineness, specific surface area and silica content depends on the combustion approach [5]. Following calcination process, the rice husk ash represents approximately 25% of the total weight of the rice husks and it contains 82–99% silica (SiO₂) in the amorphous form and minor amounts of metallic oxides (e.g.: Fe, Na, K, Ca, Mg, Mn etc.), which can be removed by acid or alkaline latching [6]. Therefore, from 1000 kg of paddy rice are produces about 200 kg (20%) of rice husk, and by combustion, which generates energy, thereof are obtained 50 kg (25%) of rice husk ash, with a concentration of 82–99% of amorphous silica, highly porous and lightweight, with a very high external surface area [2, 7, 8]. The chemical and microstructural properties of rice husk ashes may vary, depending on the rice growing lands as well as the parameters of the calcination process and other chemical treatments applied to the rice husks. Due to the high silica content, rice husk ash represents a chipper alternative for conventional silica precursors and it has extensive applicability in several industries including ceramics, construction, chemicals, electronics, etc. Therefore, various investigations have been carried out in order to adapt these properties of rice husk ash in diverse applications [2].

For instance, the chemical composition and insulation performance of rice husk gives it the property to be used as building material or as filler to enhance the mechanical properties of mortar, concrete, and polymers. Under other conditions, rice husk is an important precursor for absorbents synthesis and catalyst carriers due to its low cost and porous structure after incineration [9].

Another research presents the synthesize process of BEA and ZSM-5 zeolites, using rice husk ash containing crystalline tridymite and α-cristobalite as an alternative silica source. The ash produced from combustion of rice husk in fluidized bed reactor was characterized through various methods, demonstrating speed and continuity of the process [10].

The synthesis of ZSM-5 zeolite by hydrothermal route was conducted by Kongman Klang and Rangsiwatananon [11] using rice husk ash containing SiO₂: Al₂O₃: 98.78: 0.52 (%), thus noting that the silica source and composition of the synthesized gel strongly influenced the crystallinity, particle size, and sialilite morphology. Also, for zeolites synthesis, Ali et al. [12] used the rice husk ash, in order to investigate the Na₂O / SiO₂ ratio effect. The results clearly showed that Na + intake played a role in regulating the structure and also a role of balancing charges loads.

The objective of this work is to find out proper conditions to produce rice husk ash which could be used as silica precursor replacement in synthesis process of materials with applicability in environmental protection. Rice husk ash samples were obtained at different conditions (pre-treatments, combustion temperature) and have undergone a mechanical grinding process, in order to determine microstructural differences. The characterization of the developed raw rice husk ash samples and of the mechanical processed rice husk ash samples has been achieved through advanced characterization instruments.

2 Materials and methods

Rice husk was procured from a rice field from Romania. For the preparation of rice husk ash, hydrochloric acid (HCl 25%), oxalic acid (C₂H₂O₄ 1N) and distilled water were used during the pre-treatments of rice husks.

The rice husks were transformed into ashes through six different methods, in order to determine the optimal one (the highest SiO₂ content with proper crystallinity, microstructure and particle size distribution). Six types of rice husk ashes (identification codes: CCO1, CCO2a, CCO2b, CCO3a, CCO3b, CCO4) were thus obtained, by applying different chemical and thermal treatments to rice husks (by varying parameters such as washing steps, the stirring temperature and duration, and the thermal treatment temperature) [13].

CCO1 synthesis - rice husks are incinerated through open flame combustion (gas lamp) until complete conversion into ash, without any pre-treatment.
CCO2a / CCO2b synthesis – rice husks are washed with a sufficient amount of distilled water and dried. Subsequently, the rice husks are mixed with HCl solution at 85 °C, for 3 h, filtered with distilled water until neutral pH and dried. The final product is collected through calcination at 600 °C (for CCO2a) and 700 °C (for CCO2b), for 2 h.

CCO3a / CCO3b synthesis - rice husks are washed with a sufficient amount of distilled water, HCl solution, and again with distilled water, then dried. The rice husk is mixed again with HCl solution at 90 °C, for 2 h, then washed with distilled water until neutral pH and dried. The rice husk ash is obtained by calcination at 550 °C (for CCO3a) and 700 °C (for CCO3b), for 2 h.

CCO4 synthesis - rice husks are washed with C2H2O41N solution, dried, then incinerated through open flame combustion (gas lamp) until complete conversion into ash.

In order to characterize the obtained rice husk ashes, a series of analyses were performed: X-ray diffraction, laser granulometry and scanning electron microscopy (SEM).

X-ray diffraction studies were performed with a Bruker D8 Advance in order to obtain precise information about the chemical composition and crystalline structure of the obtained materials.

The particle distributions and sizes of solid particles in liquid media were obtained through laser diffraction using a Laser Particle Sizer ANALYSETTE 22 NanoTech analyzer.

SEM micrographs were performed on a HITACHI SU-70 FE-SEM to determine the morphology and granulometric distribution of SiO₂ crystals, as well as the interaction and formation processes of the reaction products observed in the developed materials.

3 Results and discussion
In order to determine the phase purity and crystal structure of the resulting rice husk ashes, X-ray diffraction measurements were performed on all six samples (Figure 1).

![Figure 1. X-Ray Diffraction of as synthesize samples.](image)

All samples exhibited a broad band at approximately 2θ = 22.5 °, which is the characteristic peak of amorphous silica (cristobalite in tetragonal structure). The sharpness of this peak generally increased with incineration temperature, suggesting the temperature-dependent crystallization of silica.
A small peak corresponding to carbon was observed at \(2\theta = 29^\circ\) only for CCO1 and CCO4 samples (which were incinerated through open flame combustion).

According to the literature [14-16], the carbon content is decreasing with incineration temperature from about 40% at 400 °C to less than 3% at 800 °C because of the continuous degradation of organic matters in rice husk, while the silica content simultaneously increased from 30% to more than 95%.

The XRD analyses indicate the amorphous nature of all RHA samples obtained through all synthesis approaches. In case of CCO1 sample, the diffractogram presents other two picks at \(2\theta = 27^\circ\) and \(2\theta = 37^\circ\), representing the formation of silica quartz structure. The same structure is present in the pattern of CCO4 sample too, at \(2\theta = 27^\circ\) and \(2\theta = 40.8^\circ\), but more than that, here can be observed the presence of kalisilite, due to the pre-treatment applied to the rice husks (pre-treatment with oxalic acid solution).

X-ray diffraction pattern from the four HCl leaching treatment CCO2a, CCO2b, CCO3a, and CCO3b shows smaller intensity peaks, compared to the other two samples (CCO1 and CCO4), concluding that leaching the rice husks as a pre-treatment with HCl solution can reduce the intensity of silica.

To determine the particle size distribution and the differences between the resulted raw rice husk ashes and the grinded rice husk ashes, laser granulometry measurements were performed on all twelve samples. In case of raw samples, the ashes were superficially milled in order to deagglomerate the possible formed clusters, but not to be completely transformed into powder (not to modify the particle microstructure). The particle size distribution chart for the six developed raw materials can be seen in Figure 2. In case of processed samples (grinding process – identification codes: CCO1_M, CCO2a_M, CCO2b_M, CCO3a_M, CCO3b_M, CCO4_M), the ashes were manually milled for several minutes, until complete transformation into powder. The particle size distribution chart for the six mechanical processed samples can be seen in Figure 3.
Figure 4. SEM images of the developed materials before and after mechanical processing: a) CCO1; b) CCO1_M; c) CCO2a; d) CCO2a_M; e) CCO2b; f) CCO2b_M; g) CCO3a; h) CCO3a_M; i) CCO3b; j) CCO3b_M; k) CCO4; l) CCO4_M.

It can be noticed that for all 6 raw samples, the particle size distribution ranges from 10-100 μm, with unnoticeable differences - for CCO2a, CCO2b, CCO3a, CCO3b and CCO4, the range 30-40 μm is shown as having the highest share, while for CCO1, the highest share also includes the fraction of
50 μm. On the other hand, in case of grinded samples, it can be seen a decrease in the value of highest share – for CCO3a_M the granulometric distribution varies in 0,1 – 30 μm range; for CCO4_M, the distribution range varies between 10μm and 50 μm; for the rest of the milled probes, the highest share of granulometric distribution varies in 5 – 40 μm range. It can be established that the applied pre-treatment influences to a very small extent the granulometric distribution of rice husk ashes. Compared to the raw samples, the processed samples present noticeable differences, due to the temperature and the maintenance time of the applied thermal treatment.

The obtained rice husk ashes, with high silica content (85,8 % - 99,35 %) with a decrease of metal species concentration in the resulting ashes which have been previously subjected to acid leaching (CCO2a, CCO2b, CCO3a, CCO3b and only slightly noticeable for CCO4), were characterized through SEM micrographs (Figure 4) in order to present the thermal destruction of organic matter in rice husk by forming a porous structure through the carbonization of amorphous carbon. More than that, SEM images were performed both, on raw rice husk ash samples and on rice husk ash samples after mechanical processing in order to determine differences in particles sizes and microstructures.

In case of raw rice husk ash samples (a., c., e., g., i., k.), it can be noticed a difference in terms of microstructure between the samples obtained by direct flame combustion (CCO1 and CCO4) compared to the samples obtained by calcination (CCO2a, CCO2b, CCO3a and CCO3b). In the case of samples obtained by calcination, a substantial increase in the number of pores formed in the material matrix is evidenced. This is due to the total consumption of cellulosic material at constant and maintained temperature above 550 °C (the incineration process of CCO1 and CCO4 samples was carried out until complete burning without maintenance). Between inner and outer surfaces there is a loose reticular interlayer, which is made of criss-cross plate pieces and contains a large amount of pores (around 10 μm). This structure is called reticular honeycomb structure. The reticular structure is mainly composed of protein, sugar, lignin, cellulose and some metallic oxide [4].

In the process of exposure of rice hull particles (CCO2b and CCO3b) to higher temperature (700 °C), the silica tubes remained unaffected compared to rice husk ashes obtained through the same chemical method but with a lower heat treatment applied (CCO2a and CCO3a). The observed difference is that there are a large number of pores as a result of the application of higher temperatures. Because of the enhanced thermal destruction of organic matter in rice husk, the samples calcinated at 700 °C showed a porous structure with a cross-linked heat-refractory silica framework.

The performed micrographs showed multilayered, angular and microporous rice husk ashes, explaining the considered high specific surface area, a defining aspect for this type of material, thus considered in the literature.

Due to the fact that the resulting raw ashes were not subjected to a grinding process before the microstructural characterization, the cob-shaped cellulose structure of raw rice husk was conserved for all six samples. In addition, these showed preserved needle-like protuberances because the refractory silica was mainly localized in regions corresponding to the protrusions and adjoining sloping areas.

In contrast, in the case of mechanical processed rice husk ash samples, the cob-shaped cellulose structure disappears almost completely for calcinated materials (CCO2a_M, CCO2b_M, CCO3a_M and CCO3b_M), thus confirming the complete transformation of base material and indicating that only minor thermal destruction occurred under low temperatures.

4 Conclusions
The considerable amount of carbon contained in rice husks decreased with increasing the calcination temperature. Consequently, this has led to an increase in the silica content of the ashes. In addition, increasing the temperature from direct flame combustion to 550 °C, 600 °C and 700 °C has resulted in a high porosity of the material.

The pre-treatment of rice husk caused changes in the compositional phases and crystalline structure of the samples, HCl leaching reducing the intensity of silica in the XRD pattern, forming only a cristobalite phase, while leaching with oxalic acid facilitated the persistence of K2O alkali, determining the formation of kalilite phase.
The preparation approach influences to a very small extent the granulometric distribution of rice husk ashes in a raw form. After mechanical processing, the granulometric distribution changes its highest share from an average value of 50 µm with a tendency to reach 100 µm into an average value of 30 µm with a tendency to reach 0.1-10 µm. Therefore, it can be considered that all six types of samples are suitable for subsequent applications in environmental protection in terms of particle size.

The combustion temperature applied to the rice husk samples shows an influence over the consumption of cellulosic material, determining the formation of a porous structure in the rice husk ash microstructural matrix. Thus, the calcination at 550-700 °C facilitates a substantial increase in the number of pores, in a reticular honeycomb structure.

Considering the proper compositions and microstructures of the developed materials, from both, economic and environmental perspectives, these may be a viable solution for further applications in environmental protection.

5. References

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