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Studies on silica obtained from rice husk

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Abstract

The potential and limits of rice husk to prepare relatively pure activated silica were investigated. For the activated silica, rice husk samples were submitted to a chemical pre-and post-treatment using HCl, H_2SO_4 and NaOH solutions. Samples were incinerated at 600°C under static air and flowing atmospheres (air, argon and oxygen). The product was characterized in terms of silica content, particle size distribution and morphology, specific surface area and porosity. The particle size distribution range from 0.030 to 100 μm. The structure is amorphous. The specific surface area reaches value of 321 m^2/g, porosity diameter is 0.0045 μm, specific pore volume is 4.7297 cm^3/g. Purity is 99.66% SiO_2. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: D. SiO_2; Rice husk; Structural studies

1. Introduction

Rice husk is an agricultural waste material abundantly available in rice-producing countries. They are the natural sheaths that form on rice grains during their growth. Removed during the refining of rice, these husks have no commercial interest [1]. The annual world rice production amounts to approx. 400 million metric tons of which more than 10% is husk [2]. A large quantity of husk, which is known to have a fibrous material with a high silica content, is available as waste from rice-milling industries. The major constituents of rice husk are cellulose, lignin and ash varying with the variety, climate and geographic location of growth. The white ash obtained from the combustion of this raw material at moderate temperature contains 87–97% silica in an amorphous form and some amount of metallic impurities [3].

Many authors have concluded that rice husks are an excellent source of high-grade amorphous silica [1–6]. This silica has been shown to be a good material for the synthesis of very pure silicon, silicon nitride, silicon carbide and magnesium silicide [1,7,8]. Utilization of rice husk as a resource of silica is based on removal of impurities with low effort and the high specific surface. In previous literature, they have shown that reasonably pure silica can be obtained from rice husk ash by a simple acid-leaching procedure [3].

They also have shown that, by mineral acid leaching, silica of >99% purity can be obtained by burning rice husks at 600°C under inert atmosphere [1]. Further studies investigated the effects of incineration time and temperature on the ash structure. Specific surface areas reached ~260 m^2/g (600°C) [2]. The present study strives to achieve completeness of combustion, high purity and high specific surface area at the same time in order to establish rice husk silica as a competitive product. The objective of the present work is also to make structural property studies (XRD, SEM, TEM and BET) of silica prepared from rice husk ash.

2. Experimental

2.1. Pre-treatment

The rice husks were supplied by The Trakya Region (Turkey). They were washed with water to remove dirt and other contaminants present in them and then dried in an oven-dried (Model FN 400, Nüve) at about 110°C for 24 h.

2.2. Chemical treatment

The washed and dried rice husks were submitted to different types of chemical treatment. Acid leaching was

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performed by reflux boiling in 3% (v/v) HCl and 10% (v/v) H_2SO_4 for 2 h, at a ratio of 50 g husk/l. Alkaline leaching used a 3% (v/v) NaOH solution for 24 h at room temperature (approx. 25°C), at a ratio of 50 g husk/l. After leaching, the husk was thoroughly washed with distilled water and then dried in an air oven at 110°C.

2.3. Incineration

Based on literature data, an incineration temperature of 600°C was chosen. The cleaned husks were then burned inside a muffle furnace (Model FN 100, Nüve). Four different methods were applied. First, incineration took place in a porcelain crucible for 4 h in static air. Alternatively, incineration was performed in a stainless steel tubular reactor which was 160 mm in length and 70 mm in diameter under flowing argon (1.5 l/min, for 3 h) and then flowing oxygen (1.0 1/min for 1 h). This reactor was placed horizontal inside the muffle furnace. Third, incineration took place in the same reactor under flowing air (3 l/min, for 3 h). And last, the husks were burned in the same reactor under flowing oxygen (1.0 l/min, for 2 h). Amounts of 20 g were distributed in the reactor. The reactor used for incineration is shown in Fig. 1.

2.4. Characterization

Silica contents of calcined rice husks and rice husk ashes were determined with gravimetric method. The weighed sample was thoroughly moistened in the platinum crucibles with distilled water. Four drops 1 + 1 H_2SO_4, followed by 10 ml HF were added. The mixture was slowly evaporated to dryness over a hot plate in a hood. The crucible was ignited to constant weight at 1200°C and the weight of the crucible and contents were recorded. The weight of crucible and contents after the HF treatment subtracted from the corresponding weight before HF treatment. Silica was determined as loss on volatilization.

X-ray diffractometry (XRD) diagrams of the samples were obtained with a diffractometer (Model XRD 6000, Shimadzu).

The scanning electron microscopy (SEM) examinations were performed with a SEM microscope (Model JXA 840 A, Jeol). The transmission electron microscopy (TEM) examinations were performed with a TEM microscope (Model TEM 100 C, Jeol).

The specific surface area was measured using the Brunauer–Emmett–Teller (BET) method with an adsorpmeter (Model Flow Sorb II-2300, Micromeritics).

Porosity was determined with a mercury porosimeter (Autopore II 9220).

Density measurements were done by a picnometer, pear shaped, Gay-Lussac type, with ground capillery stopper.

Determination of weight loss of sample was performed in a muffle furnace according to the static method (Thermolyne 48000 Furnace). Static weight losses analysis diagram was obtained at a heating rate of 10°C/min under air atmosphere.

Calcination was done in a muffle furnace (Thermolyne 48000 Furnace) at a heating rate of 10°C/min for 4 h at 500, 600, 700, 800°C.

3. Results and discussion

Fig. 2 shows weight losses of rice husk versus temperature. The sample weight is stabilized, after a 78% weight loss, at 500°C. The total weight loss of 78% is observed, which means that the sample obtained by burning the rice husks is constituted of 22 wt.% silica and metallic impurities and 78 wt.% H_2O and CO_2 that

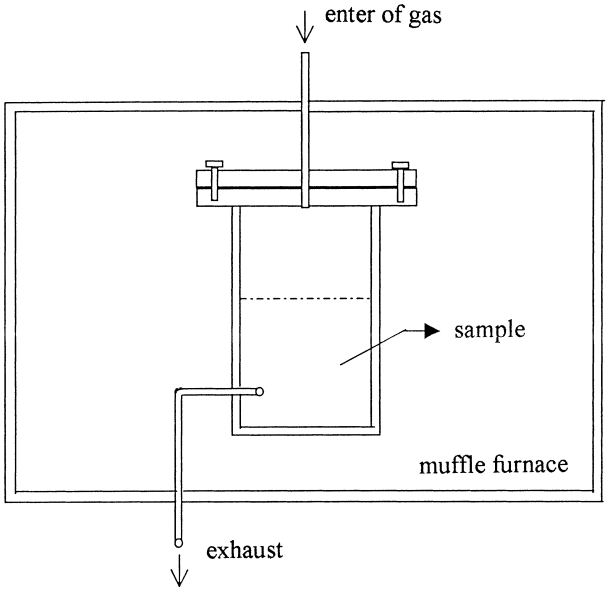

Fig. 1. The reactor used for incineration to rice husks.

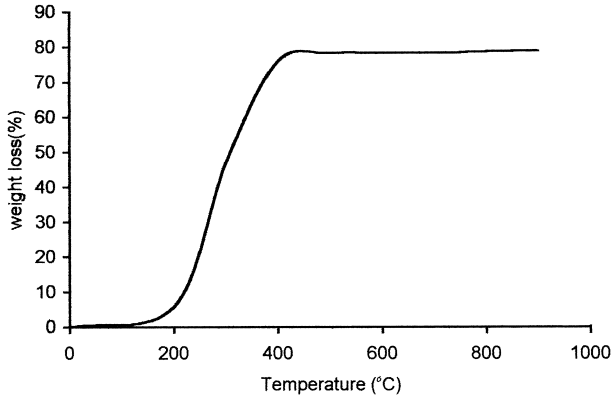

Fig. 2. Weight loss–temperature curve of rice husks.

can be removed by heating at 600°C under air atmosphere.

Density measurements and silica content of untreated rice husk and calcined rice husks at 500, 600, 700, 800°C (for 4 h) are given in Table 1.

It is seen from the table that the sample density increases with silica content. In the previous literature, it was reported that dramatic coarsening of the structure was observed at $T \geq 700$°C and the products were no longer X-ray amorphous. It transformed to cristobalite and tridymite by annealing at $T \geq 700$°C [2]. Density increased with formation crystalline silica.

In the untreated rice husk, silica content is 25. 81 wt.%. This value agrees with 24 wt.%, 400°C, that is found by the weight loss determination.

In the calcined rice husk samples at 500, 600, 700, 800°C (for 4 h, in static air) silica values increased with temperature. The untreated rice husks were calcined under different atmospheres at 600°C. Silica content of the calcined samples is given in Table 2.

The highest silica content was observed with flowing oxygen. Flowing argon + oxygen and static air values gave the similar results. It was difficult to achieve complete incineration. An increase of oxygen partial pressure helped to reduce carbon but did not completely solve the problem.

Samples treated with different ways were named as Table 3. The samples were leached in the chemical solutions before or after incineration.

The same procedures in Table 3 were repeated for all samples using static air. Static air tests gave good results as the flow tests. Especially, the leached samples were obtained as a fine white ash. Silica content in the samples is given in Table 4.

The economic compromise of a ratio of 50 g husk/l leachant yielded acceptable purity (except NaOH). The silica content of rice husk ashes was strongly depended on the type of chemical used and was best for sample G. Sample E and sample C given also high purity degrees. The ± show the standard deviation for the number of samples given in parentheses.

The XRD diagrams of samples, shown in Fig. 3, indicates that samples are X-ray amorphous. They did not show crystalline structure. The peak position was observed at $2\theta = 22°$.

The SEM micrograph of sample A and the TEM micrographs of sample A, C and G are given in Figs. 4–7. According to the SEM micrograph of sample A, obtained from the untreated rice husk; particle size distribution indicated a large scale from 0.030 to 100 μm. Average particle size was 75 μm and they were an irregular geometry and spherical morphology. The tendency to form agglomerates at the micron and under micron dimensions is seen from Figs. 4 and 5. However, the particle morphology in under micron dimensions of sample with TEM micrograph is shown in Fig. 5.

In the samples C and G treated with HCl, two different morphologies as the irregular geometry and spherical were observed. In the sample C, it was observed that the sub-micron dimensioned spherical particles intensively agglomerated on the great dimensioned shapeless particles wall and between themselves. At these, average particle size was 0.030 μm. Sample C presented a homogeneous particle distribution according to sample A. TEM micrographs of sample C is given in Fig. 6.

The particles with under micron dimensions of sample G were more dense and there were of different dimensions

Table 1
Density and silica content of calcined rice husks

Temperature (°C)	Density (g/cm^3)	SiO_2 (wt.%)
Untreated rice husk	0.559	25.81
500	1.825	83.66
600	1.923	91.50
700	1.938	91.85
800	1.960	92.90

Table 2
Silica content of calcined samples under different atmospheres

Incineration	SiO_2 (wt.%)
Static air (4 h)	91.50
Flowing air (3 h)	85.06
Flowing argon + oxygen (3 + 1 h)	91.64
Flowing oxygen (2 h)	98.32

Table 3
The treatments of sample preparation

Sample names[a]	Treatment	Treatment hour
A	–	–
B	3% (v/v) HCl (post-)	2 h (at b.p.)
C	3% (v/v) HCl (pre-)	2 h (at b.p.)
D	Distilled water (pre-)	2 h (at b.p.)
E	10% (v/v) H_2SO_4 (pre-)	2 h (at b.p.)
F	3% (v/v) NaOH (pre-)	24 h (at room temp.)
G	3% (v/v) HCl (pre- and post-)	2 h + 2 h (at b.p.)

[a] All the samples were incinerated at 600°C for 3 h under flowing argon and then 1 h under flowing oxygen.

Table 4
Silica content of rice husk ashes, standard deviation (±) and number of investigated samples (in parentheses)

Sample names	Treatment	SiO_2 (wt%)
A	–	91.50±0.5 (3)
B	HCl	95.14±0.2 (3)
C	HCl	99.16±0.1 (3)
D	Distilled water	95.48±0.2 (3)
E	H_2SO_4	99.60±0.05 (3)
F	NaOH	39.80±0.5 (2)
G	HCl (pre-and post-)	99.66±0.02 (3)

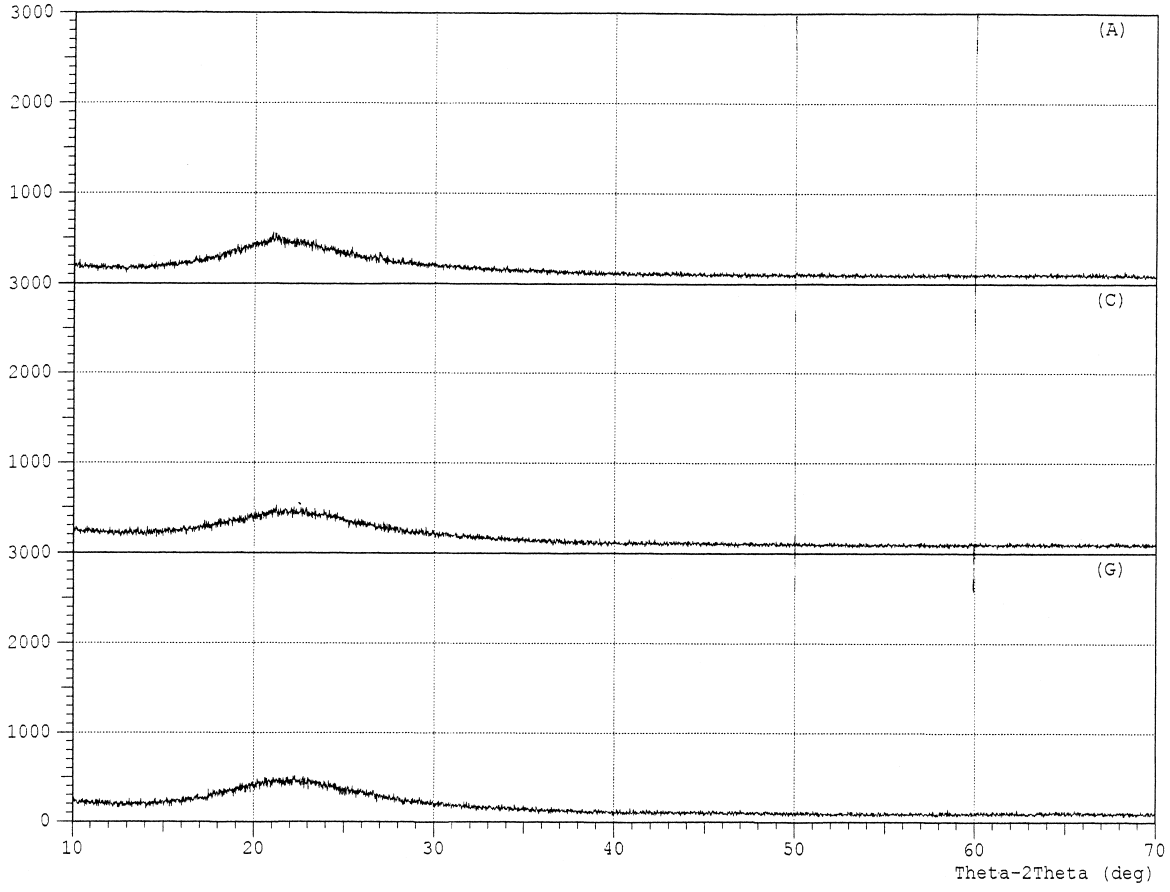

Fig. 3. XRD diagram of samples.

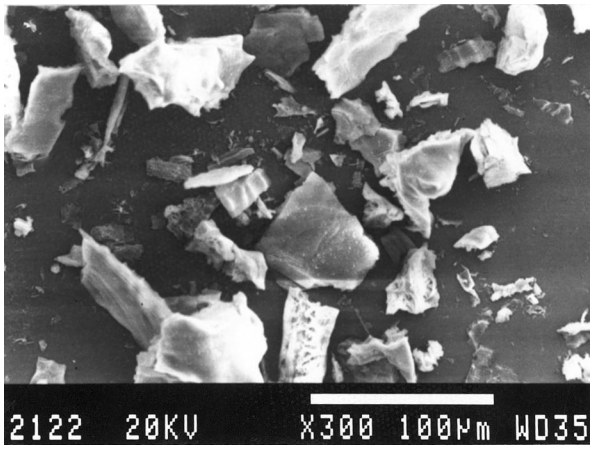

Fig. 4. SEM micrograph of silica from the untreated rice husk.

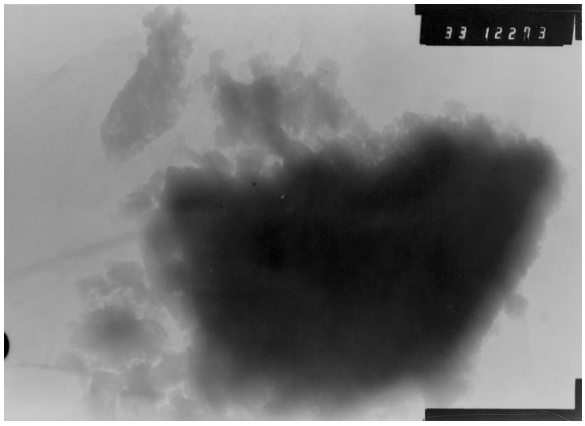

Fig. 5. The particle morphology in under micron dimensions of sample A with TEM micrograph.

compared to the sample C. Average particle size at these was 0.060 μm. At the samples C and G, particle size distribution at large particles was between 0.15 and 0.45 μm. TEM micrographs of sample G is given in Fig. 7.

BET specific surface area and specific pore volume of the calcined rice husk samples are given in Table 5.

The highest BET specific surface was found to be 321 m^2/g of sample C treated with HCl before incineration. This value is higher than the value of 260 m^2/g, measured by Real and others in 1996 [1]. Sample E treated with H_2SO_4 before incineration showed 282 m^2/g value. This was another high value for specific surface area. At the sample G treated with HCl before and after

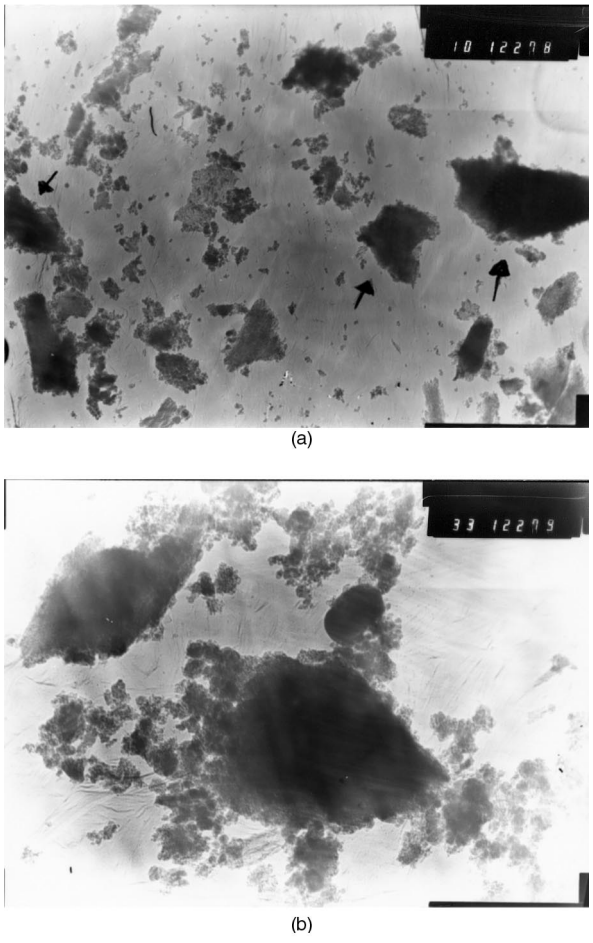

Fig. 6. TEM micrograph of sample C: (a) general and (b) high magnification.

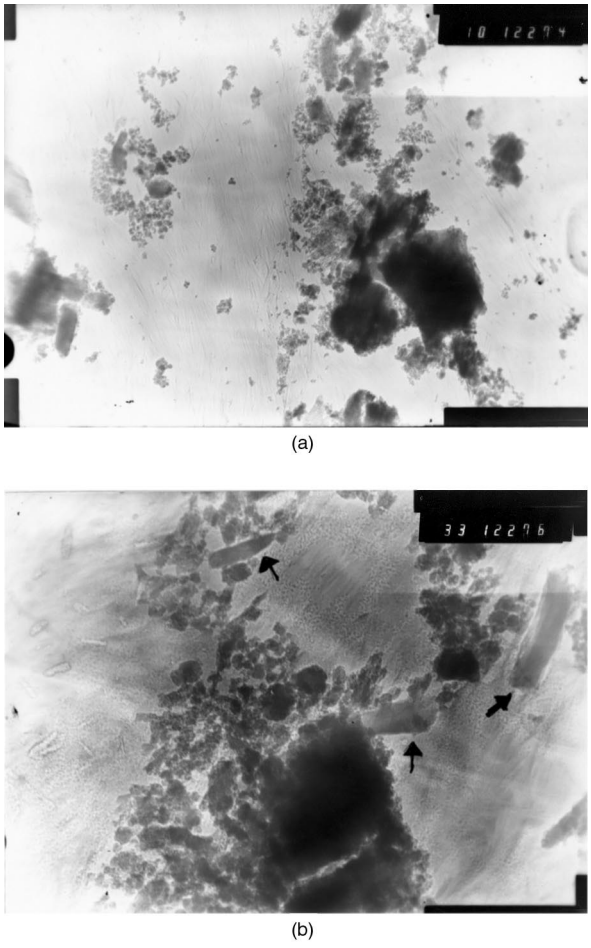

Fig. 7. TEM micrograph of sample G: (a) general and (b) high magnification.

Table 5
BET specific surface area and specific pore volume of calcined rice husk samples

Sample	Specific surface area (m^2/g)	Pore specific volume (cm^3/g)	Average pore diameter (μm)
A	63±1	–	–
C	321±1	4.7297	0.0045
D	194±1	–	–
E	282±1	–	–
G	244±1	–	–

incineration, an amorphous silica with the most purity was obtained, but its specific surface area decreases to 244 m^2/g. The smallest value of 63 m^2/g was measured with the A untreated sample. D is the sample treated with H_2O before incineration. This treatment is expected to remove the alkali ions exclusively. The BET surface area of this specimen was 194 m^2/g and this method was the least expensive way to obtain an amorphous powder (material) silica of 95.48 wt.% SiO_2 content.

Pore specific volume and average pore diameter of sample C, the highest specific surface area sample and presents homogeneous particle size distribution is also given in Table 5. The total pore volume of sample C was 4.7297 cm^3/g and average pore diameter of it was 0.0045 μm. Sample C takes place on the mesopore region with 45 Å pore diameter value.

4. Conclusion

It was shown that pure and amorphous silica with a high specific surface area can be obtained from rice husks. There was a problem for the quality of the rice husk silica. It was the tendency to form agglomerates. By a suitable sample preparation route, a size reduction could be achieved. A silica specimen that was obtained by burning the rice husks at 600°C after leaching of this raw material in HCl, presented a homogeneous particle size distribution compared to the other sample preparation techniques. The product with small particle size and high specific surface area can be use with different aims, for instance, an absorbent or catalyst support.

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