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Characteristics of rice husks for chlorination reaction

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Abstract

This paper presents a contribution to the study of the preparation of rice husk pellets containing silica and carbon. The pelletizing technique has been described in this paper with emphasis on the pretreatment of the rice husk samples: (a) to render adequate grain size; (b) for obtaining the SiO_2/C ratio to maintain a stoichiometric balance of the chlorination reactions; and (c) to obtain the desired pellet characteristics for chlorination. Pellets and rice husk powders were analyzed using optical microscopy and SEM.

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1. Introduction

During the last few decades, rice husk has been considered to be a very important raw material for obtaining solar grade silicon (Si-GS) [1–4], silicon carbide whiskers (SiC) [5–7], silicon nitride ceramics (Si_3N_4) [8,9], and in the preparation of concrete and cements for surfacing [10–13].

Rice husk is formed during the growth of rice grains in the development stage of the plant. It acquires, in its composition, cellulose, lignin, small quantities of proteins and vitamins, inorganic compounds rich in silicon and small concentrations of other metals [11].

The chemical composition of rice husk, consisting mainly of silica and carbon formed during thermal degradation of cellulose chains, has been found to be the main aspect for its use in the areas of advanced ceramics (SiC and Si_3N_4) and electrical energy generation (Si-GS). Published data show that the amount of silica and carbon present in precalcined rice husk are approximately 55% and 45% by weight, respectively, and correspond to a C:Si ratio of 4 [2].

Presently, the world production of rice is approximately 500 million tons a year containing approximately 50–100 million tons of rice husk [14]. In Brazil, the annual rice production is about 10^7 tons, equivalent to $2 \cdot 10^6$ tons of rice husk. Of this, about 300 000 tons of silica per year are extracted (this quantity depends on the soil type, plant variety and climatic conditions, etc.). Another relevant factor is its low cost compared to its large applicability; and its demand reduces environmental pollution problems.

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Among the various methods for obtaining silicon nitride, the synthesis route based on the utilization of silicon tetrachloride has been used [15]. One of the processes for obtaining silicon tetrachloride consists of chlorinating silica in the presence of a reducing agent like carbon, using chlorine gas as the chlorinating agent [16–18].

According to the silica chlorination route, control of the characteristics of the materials — raw materials and the pellets, as well as its conditioning — are of fundamental importance with respect to the overall outcome of chlorination. Taking into consideration these aspects, this paper presents a contribution to the study in which rice husk pellets containing silica and carbon are prepared by the pelletizing technique. This is the first stage of the process to obtain silicon tetrachloride by chlorination.

The use of the pelletizing technique has been described in this paper with emphasis on the pretreatments given to rice husk samples to obtain: (a) grain size distribution adequate for this technique; (b) a SiO_2/C ratio to maintain stoichiometric balance of the chemical reactions involved; and (c) the characteristics of the pellets to be chlorinated.

The chemical reaction involved in the chlorination stage is described below:

$$SiO_2 + 2C + 2Cl_2 \leftrightarrow SiCl_4 + 2CO. \quad (1)$$

2. Materials and methods

2.1. Rice husk powder preparation

The procedure for preparation of rice husk (from the Capivari region of the State of São Paulo, Brazil) powder for the pelletizing stage consisted of washing approximately 200–800 g of rice husk in distilled water followed by leaching with 1 N HCl at 60°C for 4 h to eliminate metallic impurities. The sample was dried in an oven at 80°C for 12 h, and subsequently precalcined in a resistance furnace at 300°C, 500°C and 900°C for 2 h in argon gas injected at a rate of 0.2 l/min. A precalcined sample of the husk was ground in an agate mortar and sieved to be below 150 Tyler mesh. The different pretreatment conditions (washing and leaching) and precalcination of the rice husk are shown in Table 1.

Table 1
Different experimental conditions used for pretreating rice husk

Conditions	Precalcination temperature (°C)
Washing in water	300
Washing in water + leaching with HCl	300
Washing in water	500
Washing in water + leaching with HCl	500
Washing in water	900
Washing in water + leaching with HCl	900

2.2. Rice husk pellet preparation

Three samples of precalcined rice husk powders were prepared, containing the following: (a) sample of $SiO_2 + C$ (without addition of graphite, mixture obtained after precalcination); (b) sample of $SiO_2 + C + C_{graphite}$ (with 30% excess graphite, mixture obtained after homogenization in a V-type powder mixer); (c) sample of $SiO_2 + C + C_{graphite}$ (with 50% excess graphite, mixture obtained after homogenization in a V-type powder mixer).

The three samples were pelletized using the following operational conditions: mass of rice husk $(SiO_2 + C) = 150$ g, mass of graphite $(C_{graphite}) =$ with excess carbon, 30% and 50% excess, inclination of the pelletizing plate = 60°, inclination of the scaper = 45°, initial rotational speed of the pelletizing plate = 400 rpm, final rotational speed of the pelletizing plate = 350 rpm, agglutinant concentration (sugar) = 30% in weight.

The pellets obtained were dried in an oven at 80–100°C to remove humidity. Subsequently, the pellets were calcined at 500°C to increase their strength sufficient to withstand handling in the chlorination stage. The stabilized pellets were classified according to their diameters, between 30 and 50 mm for chlorination.

2.3. Calcination of precalcined rice husk

In order to determine the mass relation between silica and carbon, precalcined rice husk samples were calcined at 700°C for 2 h in an oxidizing atmosphere to eliminate the carbon.

2.4. Characterization of the rice husk samples

The rice husk samples treated under the different experimental conditions of washing, leaching, and precalcination were characterized using X-ray fluoroscence and X-ray emission spectroscopy, for the determination of the metallic impurities present.

The physical characteristics of this material were determined by BET gas absorption technique for specific surface area and by helium gas picnometry for real density. The morphology, porosity of the pellets, and structure of the carbonized rice husk powder were determined by optical microscopy, scanning electron microscopy and by X-ray diffraction, respectively.

3. Results and discussion

Analyses for some metallic impurities present in pretreatment with water as well as acid-treated precalcined husks samples reveal that the high concentration impurities are: P, Zn, Ba, Ca, Mg and Al. Quantitative analysis carried out by X-ray fluoroscence revealed that the Si concentration was close to 99% by weight in samples that were chloride leached and 96% by weight in samples that were just washed. On the other hand, the amount of impurities decreases substantially after chloride leaching. This indicated that acid treatment of husk did have a significant effect on the composition chemical of the rice husk. Similar data were reported by Amick [2] and Chakraverty et al. [4].

In the precalcined rice husk samples at 500°C and pretreatment by washing and leaching 1 N HCl, on the average, there was a 53.7% weight loss due to volatile species consisting of water vapour, cellulose, lignin and hemicellulose.

It was observed that precalcined rice husk could be easily ground in an agate mortar. The rice husk powder was classified in grain size fractions below 150 Tyler mesh (105 μm) and the average size was of the order of 77 μm, as obtained by the X-ray sedigraph technique.

Approximately 2 kg of precalcined rice husk (1 N HCl treated) with specific area of 200 m^2/g was obtained for the chlorination step. The specific area of a rice husk treated with distilled water was less than that treated with 1 N HCl, and the value obtained was 100 m^2/g.

The real density values obtained by helium gas picnometry revealed slightly lower density (1.83 g/cm^3) for samples leached with 1 N HCl compared to those treated only with distilled water (2.05 g/cm^3).

The X-ray diffractograms of precalcined rice husk samples at 500°C are shown in Fig. 1. The diffraction pat showed in Fig. 1a indicates the amorphous and quartz structures of the precalcined rice husk treated with distilled water. Fig. 1b shows that the rice husk samples treated with distilled water and 1 N HCl had no indications of its presence in crystalline form in the sample precalcined at 500°C. This results, where the rice husk samples treated with distilled water and 1 N HCl with amorphous structures, may lead to an increase in the rate formation of silicon tetrachloride by chlorination technique. Another observation is the effect of precalcination temperature on increasing the crystallinity of untreated rice husks with HCl. It was verified that no acid treatment process also affects the increase of the degree of crystallinity of the precalcined rice husks.

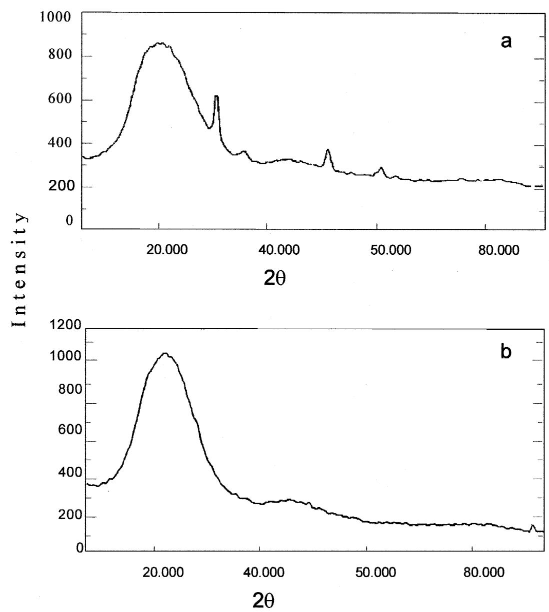

Fig. 1. X-ray diffraction patterns ofrice husk precalcined at 500°C: treated with distilled water (a); with distilled water + HCl (b).

Fig. 2. Optical micrograph showing morphology of rice husk powder.

The mass relation between SiO_2:C after three calcination tests was 0.75:1. It was found that this value was below the stoichiometric balance necessary for the reaction to take place. Thus, alternatively, graphite may be added to adjust the average carbon to silica ratio (30–50% excess graphite in weight) to promote the formation of silicon tetrachloride from rice husks.

The porosity of precalcined rice husk powders influences chlorination kinetics. The morphology determined by optical microscopy of precalcined rice husk powders revealed granules similar to miniature corncobs, as shown in Fig. 2. Fig. 3 clearly reveals this morphology, and extremely porous granules can also be seen. It is noticed that the morphology of these granules is favourable for chlorination stage.

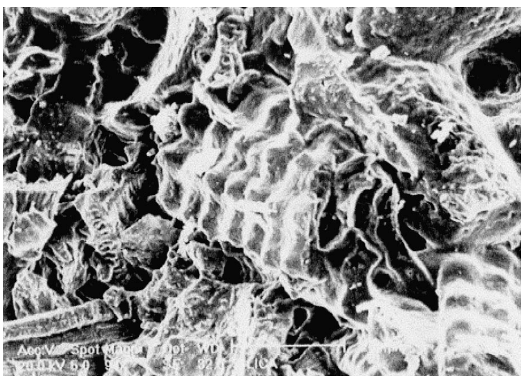

Fig. 3. Scanning electron micrograph of rice husk agglomerate.

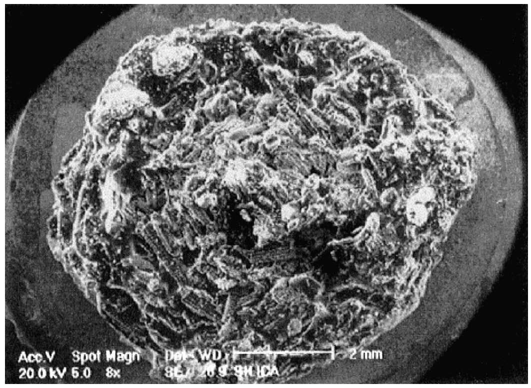

Fig. 4. Rice husk pellet.

It was also observed that the pellets obtained were quite porous, as shown in Fig. 4. Pellets with these characteristics favor chlorination reaction kinetics.

4. Conclusions

The results obtained permitted the following conclusions to be established.

- The elimination of metallic impurities in rice husk samples treated with 1 N HCl at 60°C for 4 h was possible.
- The mass relation SiO_2:C obtained after the calcination stage is below the stoichiometric relation, and therefore, in the pelletizing stage, samples were prepared with the addition of a reducing agent such as graphite.
- Characteristics such as amorphous structure, powders and pellets porosities, and sufficient handling strength of pellets, grain size distribution and specific surface area of the rice husk powders samples treated with distilled water and 1 N HCl and precalcined at 500°C were found to be quite favourable in terms of reaction kinetics, thus, permitting very satisfactory results to be obtained in the chlorination stage.

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