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Silicon tetrachloride production by chlorination method using rice husk as raw material

E.S.M. Seo*, M. Andreoli, R. Chiba

Instituto de Pesquisas Energéticas e Nucleares—IPEN/CNEN-SP, Centro de Tecnologia de Materiais, Cidade Universitária, São Paulo, Brazil

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Abstract

The rice husk is a by-product of the rice processing that contains substantially silica and carbon compounds. For this reason, it has been used as raw material to obtain silicon tetrachloride employed in several kinds of industry applications. This paper presents the characteristics of the carbonized rice husk powders and pellets as well as the SiO_2/C mass relation contained in these materials. Results showed that the addition of graphite caused the decreasing of the chlorination reaction kinetic. The best reaction yield was attained at about 1100 °C. It was also evaluated the influence of parameters such as chlorination catalysts, bed height and chlorine gas concentration. The presence of the catalyst had no significant effect on the chlorination reaction kinetic. Higher silica conversions were obtained by decreasing of the bed height.

Keywords: Chlorination; Silica; Silicon tetrachloride; Rice husk; Kinetics

1. Introduction

The chlorination method has been used to obtain high purity materials, such as solar and electronic grade silicon (99.99999% Si), silicon oxide (99.9999% Si) and silicon nitride-based ceramics (99.9% Si), due to the high purification efficiency of the products (in the range of ppb) by fractional distillation. The main products are silicon tetrachloride and chlorosilans. In chlorination reactions, it can be employed as raw materials: silicon oxide using carbon as reducing agent ($SiO_2 + C$), metallurgical grade silicon (Si-MG), silicon carbide (SiC) or silicon metal alloys (FeSi).

Silicon tetrachloride and chlorosilans have been employed as by-products in several fields like electronic, telecommunications and metallurgy. These products can be also used as advanced ceramics and in chemical and automotive industries, mainly on the manufacture of optical fibres, cutting tools, components of internal combustion engines, high speed ball bearings, mechanical seals, photovoltaic cells, integrated circuits, transistors, thyristors and chips.

Several routes for the silicon tetrachloride production have been reported in the literature, including the silica chlorination using carbon and chlorine gas as reducing and chlorinating agent, respectively [1–3].

The present paper describes the chlorination processes using rice husk, as raw material, due to its chemical composition. The rice husk is constituted mainly by silica and carbon, originated from the thermal decomposition of cellulose chains. As it can be verified in the literature, the silica and carbon contents in a carbonized rice husk are 55 and 45 wt.%, respectively. The C/Si ratio is 4/1 [4].

The rice husk has been considered attractive for the preparation of several materials such as silicon carbide whiskers [5–7], silicon nitride [8,9], solar grade silicon [4,10–12] and concrete and cements for surfacing [13–16].

In this context, this paper presents the characterization of the rice husk powders and pellets and the chlorination kinetic studies. It was studied the influence of parameters, such as temperature, reducing agent, catalysts and bed height, on the kinetic of the chlorination reaction.

2. Experimental procedure

Samples of carbonized rice husk pellets ($\phi = 3$–5 mm) were weighted to obtain an established bed height and introduced into the reactor previously filled with argon. By the time the test temperature was reached, the argon was replaced for the chlorine gas at prefixed conditions: gas flow of

* Corresponding author. Tel.: +55-11-3816-9364; fax: +55-11-3816-9370.
E-mail addresses: esmiyseo@net.ipen.br, esmiyseo@baitaca.ipen.br (E.S.M. Seo).

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Table 1
Experimental conditions of the chlorination process

Parameter	Conditions
Temperature (°C)	700, 900, 1100
Bed porosity	0.6355 and 0.6383
Bed height (mm)	5 and 10

4.0 l/min at a pressure of 1 atm for a dwell time of 5–50 min. At the end of the chlorination test, chlorine gas flow was interrupted and substituted by argon gas. The argon flow was maintained for 10–15 min and used to cool the samples and to purge the chlorination line. Finally, the bed was removed from the furnace and cooled in a desiccator. Quantitative analyses were performed.

Table 1 shows the experimental conditions employed in the chlorination reaction.

The fraction of converted silicon (χ), as a function of the time, was determined using the following equation:

$$\chi = \frac{m^0_{SiO_2} - m_{SiO_2}}{m^0_{SiO_2}} \qquad (1)$$

where $m^0_{SiO_2}$ is the initial mass of the rice husk pellets ($SiO_2 + C$) (g); m_{SiO_2} the mass of the rice husk pellets ($SiO_2 + C$), at a specific reaction time (g).

The experimental setup, used in the chlorination tests, is presented schematically in Fig. 1.

3. Results and discussion

3.1. Rice husk powder and pellets characterization

The rice husk specimen, that was leached with HCl (1 N) and carbonized at 500 °C, was characterized by X-ray fluorescence analyses to determine the metallic impurities contents. Results are shown in Table 2. It can be observed that P, Ca, Fe and K were the elements found at higher concentrations. The silicon content was at about 99 wt.%. The SiO_2/C mass relation, calculated from three calcination tests at 900 °C, was 0.75/1. This value is below the stoichiometric proportion necessary for the reaction to take place.

Physical characteristics of the powder (size <105 μm) were evaluated as a function of surface area values obtained by gas adsorption technique (BET), real density values determined by helium gas picnometry and granulometric distribution performed by sedimentation analysis (X-ray Sedigraph). The results were the following: 200 m^2/g, 1.83 g/cm^3 and 77 μm (agglomerate mean size), respectively.

X-ray patterns of the rice husk sample, treated with distilled water and HCl (1 N), are presented in Fig. 2. It was noticed that no crystalline phase was found. The presence of the amorphous structure contributes to the improvement of the chlorination reaction kinetic.

Fig. 3 shows the powder morphology of the rice husk carbonized at 500 °C, obtained by scanning electron microscopy (SEM). It can be observed that the granules are extremely porous. According to Rodrigues and Martins [17],

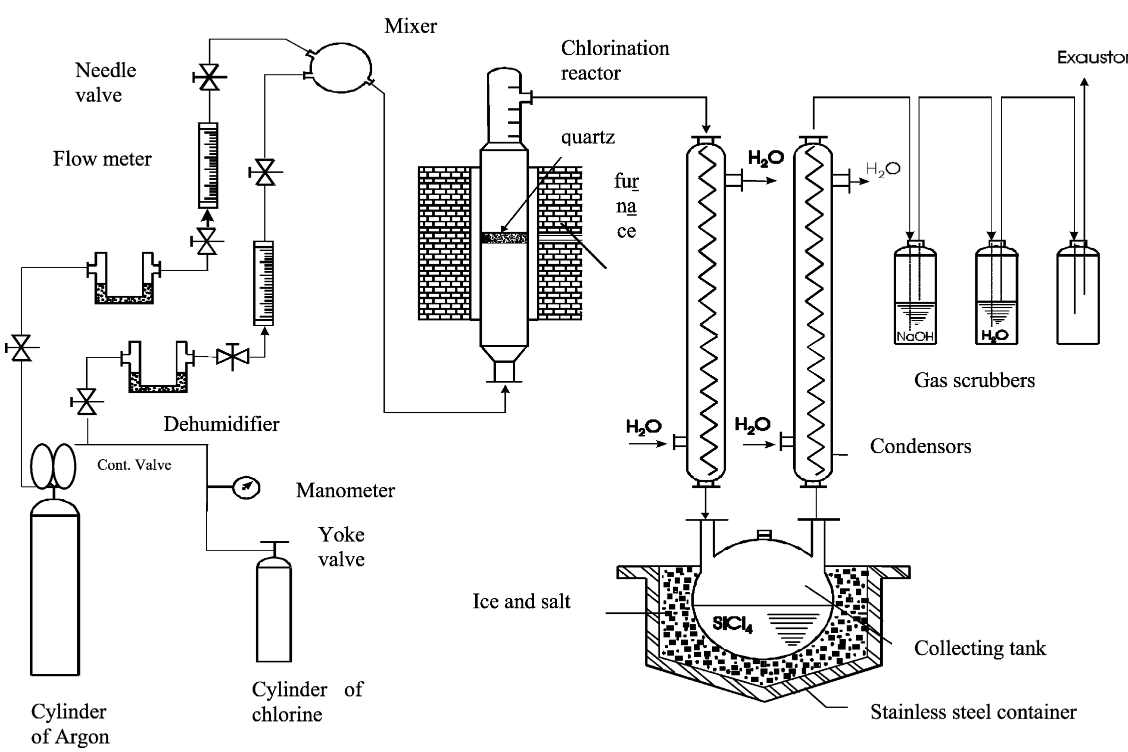

Fig. 1. Schematic representation of the experimental setup.

Table 2
Chemical composition of the carbonized rice husk

Si	P (%)	Ca (%)	Fe (%)	K (%)	S (ppm)	Na (ppm)	Cr (ppm)	Zn (ppm)	Ni (ppm)	Ti (ppm)	Mn (ppm)	Al (ppm)	Cu (ppm)	Mg (ppm)	Zr (ppm)
Base	0.35	0.23	0.84	1.36	821	506	206	221	141	175	133	55	95	36	14

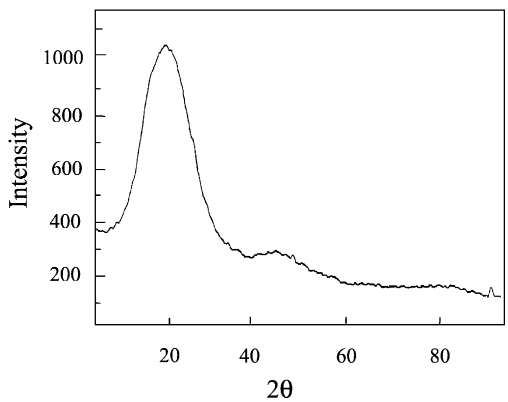

Fig. 2. X-ray patterns of the rice husk specimen ($SiO_2 + C$) carbonized at 500 °C, without graphite addition.

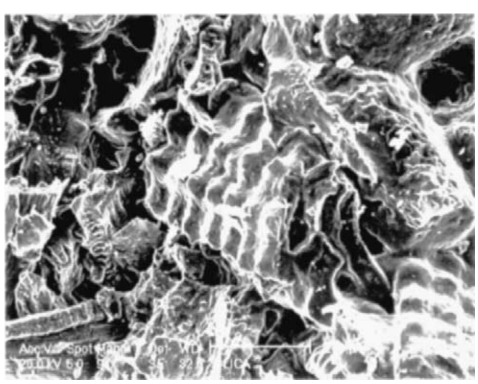

Fig. 3. SEM micrograph of the rice husk, carbonized at 500 °C.

the presence of high porosity is a typical feature of samples that contain no organic polymers. This characteristic favours the chlorination reaction.

As it can be observed in Fig. 4, the pellets with diameters in a range of 3–5 mm are also quite porous. This kind of rice husk pellets benefits the chlorination kinetic.

Those rice husk pellets, mentioned above, were submitted to the chlorination, according to the reaction:

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

3.2. Influence of parameters, such as reducing agent concentration, temperature, bed height and catalysts, on the chlorination reaction kinetic

In gas–solid reactions, that involve two different solids and a gas, the mass relation between these two solids is an important variable in a kinetic study. For this reason, if the adopted reducing agent was solid, as in the present paper, the influence of its concentration should be verified.

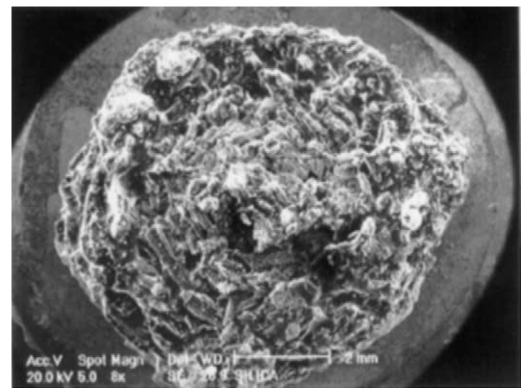

Fig. 4. SEM micrograph of a rice husk pellet.

This study has to consider some changes that could interfere in the interpretation of the experimental results. These statements are related to the differences between the two solids (density values and crystalline structures), caused by the graphite addition. The graphite contents were approximately 30 and 50 wt.%, as a function of the initial mass of carbonized rice husk ($SiO_2 + C$).

In reducing chlorination reactions, an increase in the reducing agent concentration results in the increasing of the initial reaction speed until a maximum value is reached. On the other hand, additional increases could lead to the reaction speed decrease. This behaviour is typical for tests carried out in fixed bed, due to the optimum contact area between the solids, per unit of volume [18,19].

Chlorination experiments were performed using three different sets of samples: without graphite addition, with 30 and 50 wt.% in excess of graphite. Reactions took place in a temperature range of 700–1100 °C for 30 min, employing chlorine flow of 4.0 l/min and a bed height of 5 mm. Fig. 5 shows that higher SiO_2 conversions were attained with specimens without graphite addition. The carbon content of these pellets was only that contained in the rice husk. The powders presented an amorphous phase. With reference to the samples with excess of carbon, it can be noticed that no significant changes occurred on silica conversion values at temperatures below 1100 °C. The increasing of the reducing agent content caused lower conversions due to the crystallinity difference between the carbon contained in the rice husk and the graphite. Ojeda et al. [20] have been studied the effect of reducing agent on the MoO_3 chlorination. It was observed that the use of carbon black as reducing agent in a MoO_3/C ratio different from the molar relation (1/3 to

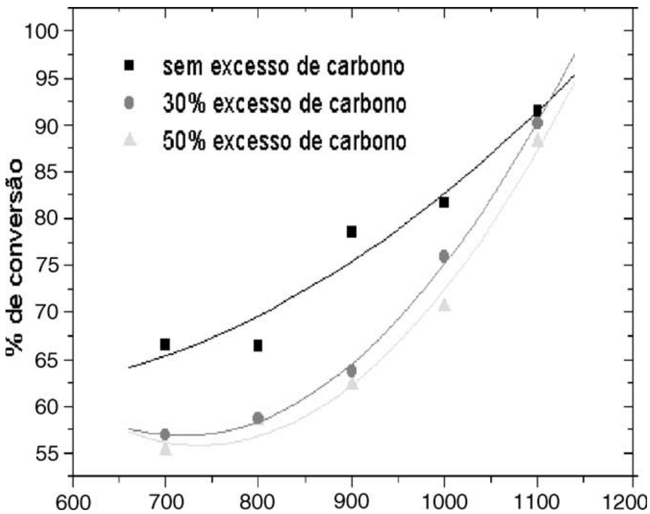

Fig. 5. Effect of the reducing agent concentration on the kinetic reaction.

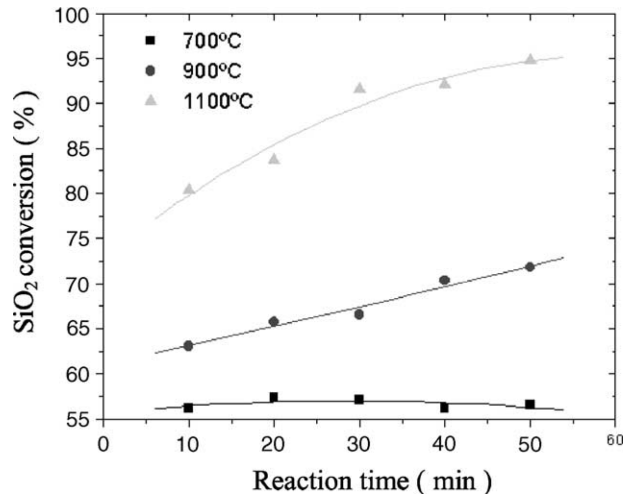

Fig. 7. Influence of the temperature on the reaction kinetic.

1/4) causes the decreasing of the MoO_3 conversion values. The paper presented by Mezzavilla et al. [21] shows that the reducing agent affects strongly the conversion values only for the chlorination tests using NiO and CuO at 800 °C. It was verified that an increasing in the carbon amount exerts no significant influence mainly at 1000 °C. These results are very similar to those obtained in the present paper [21].

The effect of the bed height on reaction kinetic was evaluated using the following experimental conditions: temperature in a range of 700–1100 °C, dwell time of 30 min, chlorine flow of 4.0 l/min, bed height of 5 and 10 mm with bed porosity of 0.6355 and 0.6383, respectively. Results are presented in Fig. 6. It was considered that the small bed height was the responsible for the high silica conversion obtained for the sample containing $SiO_2 + C$. Although the bed porosities were quite similar for the bed height of 5 and 10 mm, it was observed that the amount of converted silica was proportional to the increasing in the reaction temperatures only for the smaller bed height. It was concluded that the larger mass (higher bed height) causes different effects at operational conditions due to the longer time expended by chlorine gas to reach the whole reactional layer of the bed. It was verified that the bed height had no substantial influence at higher temperatures. The conversion values were similar (90–93%). Seo [22] has been reported similar studies about the influence of the bed height on the chlorination kinetic.

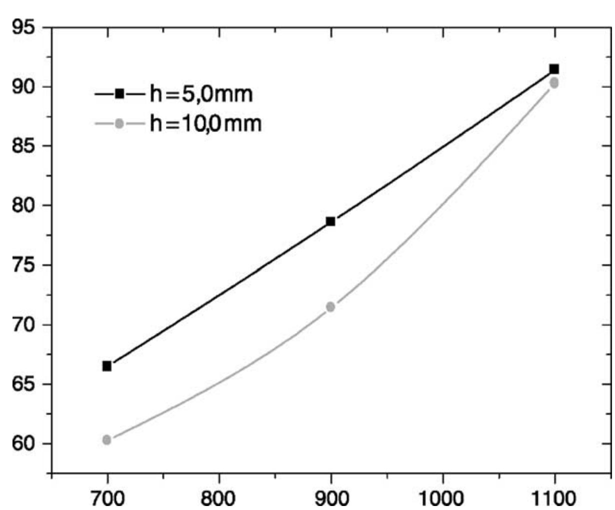

Fig. 6. Influence of the bed height on the chlorination kinetic.

Conversion curves as a function of the time (Fig. 7) illustrate the chlorination kinetic of carbonized rice husk pellets without graphite addition. The experiments were carried out according to the conditions:

- temperature (°C): 700, 900 and 1100;
- bed height (mm): 5.0;
- porosity: 0.6355;
- Cl_2 pressure (atm): 1.0; and
- Cl_2 flow (l/min): 4.0.

These experiments revealed that temperature increasing caused high values of silica conversion. At lower temperatures (700 °C), the highest conversion value (time ∼50 min) decreased to lower values (60%). The silica conversion was better at higher temperatures. It varied from 65 up to 70% and from 80 up to 95% at 900 and 1100 °C, respectively.

Fig. 8 shows the plot of Ln k versus $1/T$, that was constructed using the Arrhenius equation ($k = k_0\, e^{E_a/RT}$).

The calculated activation energy value was 130.35 kJ/mol. According to [23], the value of the activation energy has to be above 40 kJ/mol to characterize the chemical control. Mezzavilla et al. [21] has shown that the mechanism of the reaction control was considered as diffusional for some metal oxides.

Kratel and Loskot [3] have studied the chlorination of silica contained in diatomaceous earth. It has been shown that the presence of a catalyst improved the reaction kinetic at temperatures between 700 and 900 °C.

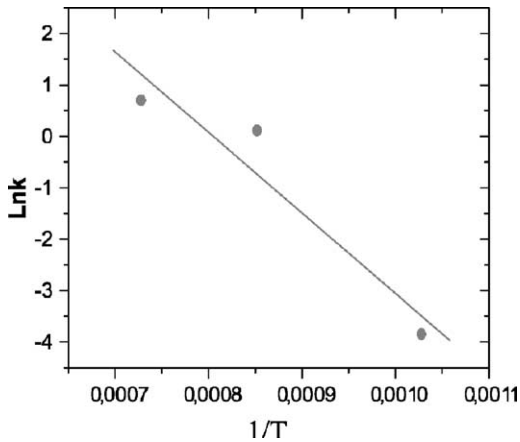

Fig. 8. Ln *k* versus 1/*T* curves of the carbonized rice husk pellets without graphite addition.

In the present paper two kinds of catalysts, CuO and TiO_2, were studied. Chlorination reactions were performed at temperatures between 700 and 1100 °C for 30 min, using as samples, pellets without graphite addition in a bed height of 5 mm. The chlorine flow was 4.0 l/min. The results are presented in Fig. 9. The conversion values were lower than those obtained without a catalyst. It was concluded that the use of CuO and TiO_2 as catalysts had no significant effect on the reaction kinetic of the rice husk pellets. It can be noted in this figure that the conversion values of SiO_2 in a presence of catalysts were low, however this behaviour has been changed as the temperature increases (curve lines). At these conditions, it was considered that the reaction speed was lower. This behaviour has been attributed to the different physical characteristics of the starting raw material such as density, granulometry and surface area. With reference to surface area, Gimenes and Oliveira [24] have shown that this characteristic is critical for the chlorination process. Besides changes on particle morphology could occur during the pellets chlorination [24].

It was also noticed that at high temperatures (1100 °C), the silica conversion values (90%) were similar for the three samples. Therefore, it was concluded that the temperature affects substantially the reaction kinetic, mainly above 1050 °C.

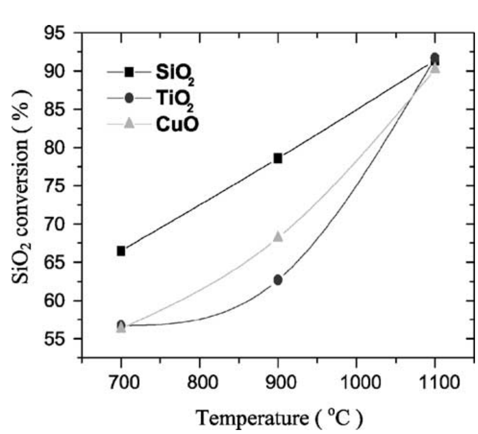

Fig. 9. Influence of the catalysts on the reaction kinetic.

4. Conclusions

The obtained results lead to the following conclusions:

(i) High silica conversion values are verified for the specimens of rice husk pellets without graphite addition.
(ii) The amorphous structure of the rice husk pellets improves the reaction kinetic.
(iii) An increase in the reaction temperature and a decrease in the bed height result in an increasing of the silica conversion values.
(iv) The influence of the temperature, within the evaluated range, is responsible for the high value of activation energy (130.35 kJ/mol), typical of chemical control.
(v) At temperatures below 1050 °C, the use of catalysts (CuO and TiO_2) has no significant effect on the reaction kinetic.
(vi) Considering the conversion of the silica contained in rice husks, above 1050 °C, the influence of the temperature is greater than the effect of the use of catalysts.

Acknowledgements

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