Synthesis of silicon carbide from rice husk

(Síntese de carbeto de silício a partir de casca de arroz)

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Abstract

This is a study about the synthesis of SiC from rice husk. The SiC production was carried out in two stages, the first one being the rice husk carbonization under vacuum, at the temperature range from 270 to 650 °C, and the second stage was the pyrolysis of the carbonized rice husk, at the temperature range from 1300 to 1800 °C and 120 min isotherms. The rice husk was characterized by X-ray fluorescence, and the reaction products were characterized by X-ray diffraction and scanning electron microscopy. The temperature influence on pyrolysis was demonstrated. SiC formation occurred in samples treated over 1600 °C, while at lower temperatures, it was possible to observe the secondary formation of cristobalite, tridymite, and quartz. In this study, it was possible to calculate the yield of SiC production as a function of the pyrolysis temperature of the carbonized rice husk.
Keywords: silicon carbide, SiC, rice husk, pyrolysis.

Resumo

Neste estudo, a casca de arroz foi utilizada para a síntese de SiC. A produção do SiC foi realizada em duas etapas, sendo a primeira etapa a carbonização da casca de arroz sob vácuo, variando-se a temperatura de 270 a 650 °C, e a segunda etapa a pirólise da casca carbonizada, nas temperaturas de 1300 a 1800 °C e isotermas de 120 min. A casca de arroz foi caracterizada por fluorescência de raios X e os produtos da reação foram caracterizados por difratometria de raios X e microscopia eletrônica de varredura. A influência da temperatura de pirólise foi demonstrada. A formação do SiC ocorreu nas amostras tratadas a partir de 1600 °C; em temperaturas inferiores observou-se a formação secundária de cristobalita, tridimita e quartzo. Neste estudo, foi possível calcular o rendimento da produção do SiC em função da temperatura de pirólise da casca de arroz carbonizada.
Palavras-chave*: carbeto de silício, SiC, casca de arroz, pirólise.*

INTRODUCTION

Silicon carbide (SiC) is one of the most important ceramic materials which are produced on a large scale. It has many industrial applications due to its high hardness, thermal and electrical conductivity, excellent corrosion, and thermal shock resistance [1, 2]. Its main applications are as structural materials, abrasives, refractories, electronic components, and nuclear reactors. The main method of SiC synthesis is a carbothermal reduction known as the Acheson process, which is an energy-intensive process making SiC a high-cost product [3]. Over the past 4 decades, many researchers have studied the use of rice husk as an alternative raw material for silicon carbide [3-13]; Lee and Cutler were the first two scientists to synthesize SiC from rice husk [14]. The benefit of using rice husk as a raw material is its low cost since in most cases the husk is considered a waste [15]; also SiC formation occurs at lower temperatures (1200 to 1500 °C) when compared to the reactions between solid quartz and graphite (1200 to 2000 °C); according to Eqs. A to C [16-18], this is due to the high surface area of the rice husk and the presence of an ionic mixture between silica and carbon in its composition.

$$SiO_{2(s)} + 3C_{(s)} \rightarrow SiC_{(s)} + 2CO_{(g)} \quad (A)$$

$$SiO_{2(s)} + 2C_{(s)} \rightarrow Si_{(s)} + 2CO_{(g)} \quad (B)$$

$$SiO_{2(s)} + C_{(s)} \rightarrow SiO_{(g)} + CO_{(g)} \quad (C)$$

Rice is one of the most consumed food in the world; according to the United States Department of Agriculture (USDA), the 2017/2018 world harvest was estimated at about 481.2 million tons [19]. China is the world's largest rice producer, and its harvest for 2017/2018 is estimated at 144 million tons. For Brazil, the estimate is 11.87 million tons [20]. As the husk represents about 22% of the grain weight, Brazil generated nearly 2.6 million tons of waste in 2018. Rice husk contains cellulose as its main constituent, an organic material that generates carbon when thermally decomposed in a reducing atmosphere, also has a high silica content (13% to 29% by weight). The ash is mainly composed of silica (87% to 97% by weight), small amounts of alkali, and traces of other elements [21]. SiC formation usually occurs in two stages. First, the rice husk is pyrolyzed in a reducing atmosphere at temperatures between 700 and

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900 °C; the product of this decomposition is then treated at temperatures around 1500 °C in an inert or reducing atmosphere [22]. Krishnarao and co-authors conducted several studies on the silicon carbide production from rice husk pyrolysis, in vacuum [22-24] and argon atmosphere [6, 25]. In one study, they found that the maximum formation of filament-shaped silicon carbide occurred in samples treated at 1320 °C, and, as the pyrolysis temperature increased, there was a tendency for filament recrystallization; at 1510 °C, the product became mainly particulate [5]. They also studied the inclusion of additives such as silicon nitride (Si_3N_4) [23], cobalt chloride ($CoCl_2$) [26], and cobalt [27] in the silicon carbide production. Recently, Li et al. [11] presented a synthesis route to obtain nanostructured SiC powder by microwave heating using rice husk as raw material. The carbothermal reduction reaction was performed at 2.45 GHz in an argon atmosphere. Gorzkowski et al. [28] also demonstrated that large amounts of β-SiC nanostructures can be obtained by pyrolysis of rice husk in a single step under controlled temperature (1375 °C) and atmosphere (argon) conditions.

Rice husk is still an environmental problem today, as not all waste generated is disposed of properly, especially in countries that produce large amounts of rice, such as China, India, and Brazil [4, 16]. On the other hand, the silicon carbide production industry requires a source of high-purity silica and carbon. The most critical SiC manufacturing issues in recent years have been the cost and availability of coke and silica, the cost of electricity, and environmental considerations [29]. The viability of rice husk would minimize the environmental impact generated by reducing husk disposal and quartz extraction. The main objective of this study was to produce pure silicon carbide, without residual silica and graphite, and for this, the process conditions such as SiO_2/C molar ratio and pyrolysis temperature were adjusted. The syntheses were performed with excess carbon to obtain a CO-rich atmosphere to produce a SiC without silica. In most cases, a chemical process with hydrofluoric acid is performed on the SiC to remove residual silica; in this study, this step was not performed. In this study, it was also possible to calculate the yield of SiC production from the rice husk.

EXPERIMENTAL PROCEDURE

Carbonization of rice husk (CRH): the rice husk (RH) used in this study was collected at a rice mill in Guaratinguetá, Brazil. The rice husk was sieved to remove possible residues, and its chemical composition was analyzed by X-ray fluorescence spectroscopy (PANalytical, Axios Max). Thermogravimetric analysis was performed on a simultaneous thermal analyzer (Netzsch, STA 449F3) with a heating rate of 10 °C/min from 25 to 1200 °C under nitrogen flow. SiC synthesis from rice husk was performed in two steps. First, the rice husk was carbonized under vacuum at different temperatures. In this first step, it was possible to adjust a SiO_2/C molar ratio as a function of temperature. In this study, a carbonized rice husk containing an excess of carbon was produced, and pyrolysis was used in the second step. The carbonization of RH cellulose in carbon was performed in a stainless-steel reactor for 45 min under vacuum (680 mmHg) at 7 different temperatures, ranging from 270 to 650 °C (CRH). The resulting carbon content in these samples was determined by heat treatment at 700 °C for 120 min in an oxidizing atmosphere.

Synthesis of silicon carbide by carbothermal reduction: for the SiC synthesis, only the carbonized husk was used, which was placed in a small graphite crucible with a lid. This set was put inside a bigger crucible and covered with graphite powder and heated in an oven (Thermal Technology, Astro 1000-4650-FP20). The pyrolysis was performed in a closed graphite crucible containing the sample in order to maintain the atmosphere rich in CO. Heat treatments were performed at 6 different temperatures (1300, 1400, 1500, 1600, 1700, and 1800 ° C) with a heating rate of 20 °C/min and 120 min isotherms. Heating was performed under vacuum; upon reaching the maximum temperature, the vacuum was broken with argon, maintained during treatment, and then cooled until reaching 70 °C. After synthesis, the obtained products were treated at 700 °C for 24 h to remove residual carbon. Fig. 1 shows the flow chart of the SiC production from rice husk.

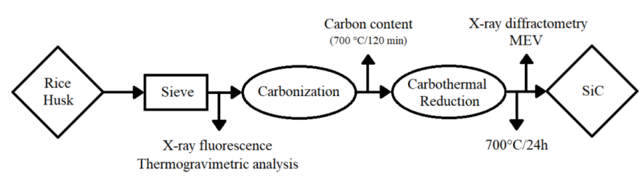

Figure 1: Flowchart of the SiC production from rice husk.
[Figura 1: Fluxograma da produção de SiC a partir da casca de arroz.]

Analysis of the crystalline phases by X-ray diffractometry of the powder after synthesis was performed using CuKα radiation (λ=1.5406 Å) with nickel monochromator and PIXcel 3D detector, with a step size of 0.01° and 2θ ranging from 10° to 90° in a diffractometer (PANalytical, Empyrean) with a software (PANalytical, HighScore Plus) for the qualitative and quantitative determination of the formed phases. The phases quantification was performed by the Rietveld method. The microstructure was investigated with a scanning electron microscope (SEM) equipped with a dispersive energy spectrometer (Hitachi, TM 3000).

RESULTS AND DISCUSSION

Characterization of the rice husk (RH): Table I shows the result of a chemical analysis of rice husk. This husk had about 10% of SiO_2 in its composition and approximately 1.7% of other elements, which were considered impurities.

The loss on ignition was 88.30%; therefore, the ash content was 11.70%. The silica content was in agreement with the literature. According to [9], the silica content in RH ranges between 8% (fresh RH) and 18% (stored RH).

Table I - Chemical composition of rice husk ash (wt%).
[Tabela I - Composição química da cinza de casca de arroz (% em massa).]

Compound	With LOI	Without LOI
SiO_2	10.56	90.3
Na_2O	0.27	2.3
K_2O	0.25	2.1
SO_3	0.18	1.5
CaO	0.11	0.9
P_2O_5	0.08	0.7
MgO	0.04	0.3
MnO	0.04	0.3
Al_2O_3	0.01	0.1
Fe_2O_3	0.01	0.1
Cl	0.15	1.3
Total	11.70	100.0

LOI - loss on ignition.

Fig. 2 shows the thermogravimetric curves of the rice husk *in natura*, where it may be observed that rice husk mass loss can be divided into three temperature ranges. The first, with a 10% loss, occurred up to 200 °C and corresponded to the moisture incorporated in the rice husk. The second mass loss of about 54% occurred in the range between 200 and 360 °C and was related to the decomposition of the hemicellulose and most of the cellulose. Lignin decomposition occurred between 360 and 525 °C, while the total thermal decomposition of the rice husk occurred below 700 °C, corroborating the results in [30].

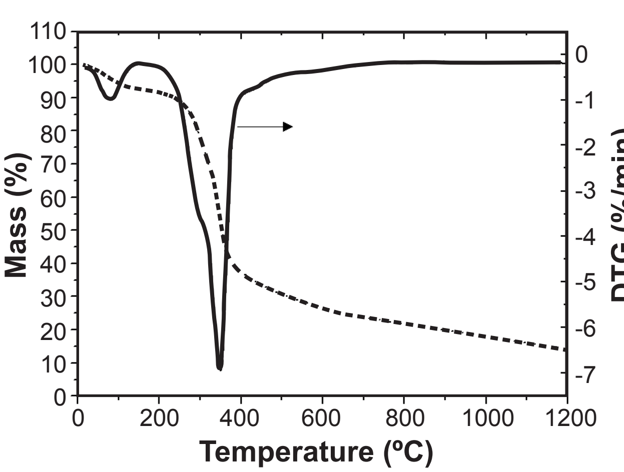

Figure 2: Thermogravimetric curves of rice husk.
[Figura 2: Curvas termogravimétricas da casca de arroz (RH).]

Characterization of carbonized rice husk (CRH): Fig. 3 shows the relationship between carbon and silica contents of the carbonized rice husk (CRH) samples, determined by oxidation at 700 °C for 120 min. The silica content was considered as 90.3% of the remaining mass after oxidation, according to the results in Table I. It may be observed that as the carbonization temperature increased, there was an increase in mass loss and, consequently, an increase in the silica concentration of the sample. In this study, a rice husk carbonized at 400 °C containing approximately 61% carbon and 35.4% silica was used for silicon carbide synthesis, therefore, with a SiO_2/C molar ratio of 0.12, resulting in approximately 3 times the stoichiometric amount of carbon required to form SiC according to the Eq. A. Krishnarao and co-authors used a black rice husk ash containing 53 wt% of carbon and 47 wt% of SiO_2 [5], and a raw rice husk with 85 wt% of organic material and 15 wt% of SiO_2 [6, 31]. Moustafa et al. [32] used a cooked rice husk containing about 40% of carbon.

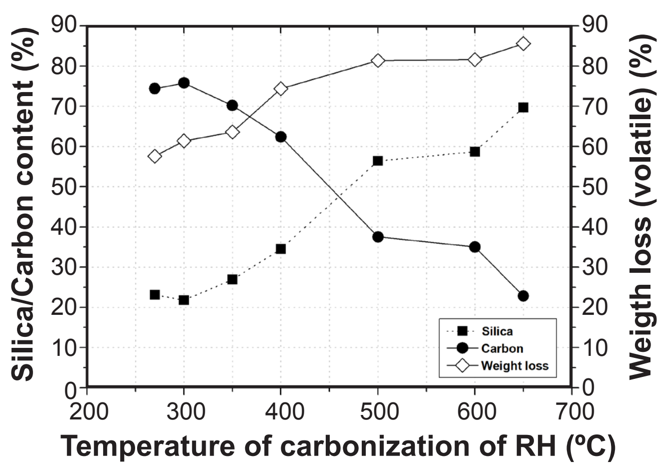

Figure 3: Carbon and silica content as a function of the carbonization temperature of RH.
[Figura 3: Teor de carbono e sílica em função da temperatura de carbonização da RH.]

Synthesis of silicon carbide by carbothermic reduction: Fig. 4 shows the percentages of residual masses obtained after synthesis and heat treatment for carbon decomposition, therefore, the yield is the sum of SiC and unreacted SiO_2. It was observed that about 29.9% to 43.5% of the initial mass was converted into a final product, a result well below the theoretical conversion values (Fig. 4). No data were found on the yield of SiC production from rice husk. The theoretical conversion was estimated, considering that the carbonized rice husk used in the pyrolysis contained 61% C and 35.4% SiO_2. For pyrolysis, 1.4 g of carbonized rice husk was used; therefore, the sample contained 0.854 g C and 0.4956 g SiO_2. According to Eq. D, reacting 0.4956 g of SiO_2, 0.297 g of 3C, and 0.557 g of excess C resulted in 0.33 g of SiC, 0.46 g of CO, and 0.557 g of unreacted C; therefore, the mass of solid products was 0.887 g (65.7%).

$$SiO_{2(s)}+3C_{(s)}+C_{(s)excess} \rightarrow SiC_{(s)}+2CO_{(g)}+C_{(s)} \quad (D)$$

Fig. 5 shows the X-ray diffractograms of the phase transformation evolution of the carbonized rice husk at 400 °C, after pyrolysis at 1300, 1400, 1500, 1600,

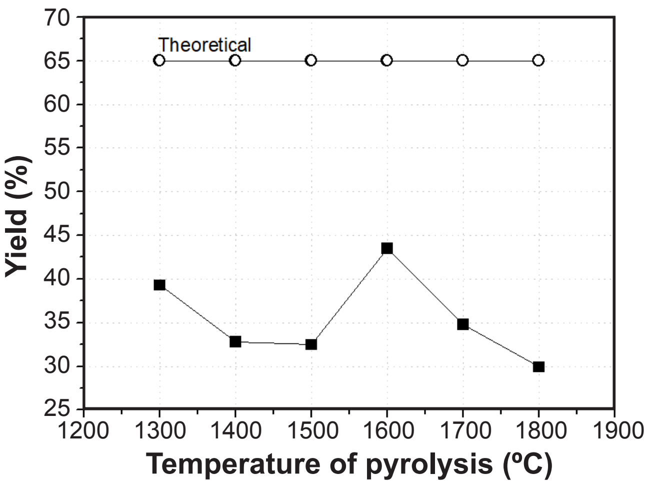

Figure 4: Yields from pyrolysis reaction.
[Figura 4: Rendimento da reação de pirólise.]

1700, and 1800 °C with the excess carbon being removed by calcination. In pyrolysis up to 1500 °C, SiC formation was not evidenced, only the polymorphic phases of SiO_2 were detected in the forms of cristobalite (ICSD 01-076-0935), tridymite (ICSD 01-075-0638), and quartz (ICSD 01-086-1562). SiC formation was observed from 1600 °C, but still with the presence of SiO_2. Pure SiC formation occurred only from 1700 °C. The carbide formed was mostly in the β-SiC form (ICSD 01-075-0254); however, traces of α-SiC (ICSD 01-089-2213) were also observed. The final yield (Fig. 5) at 1700 °C was higher (34.8%) than at 1800 °C (29.9%), due to possible decomposition of SiC at 1800 °C.

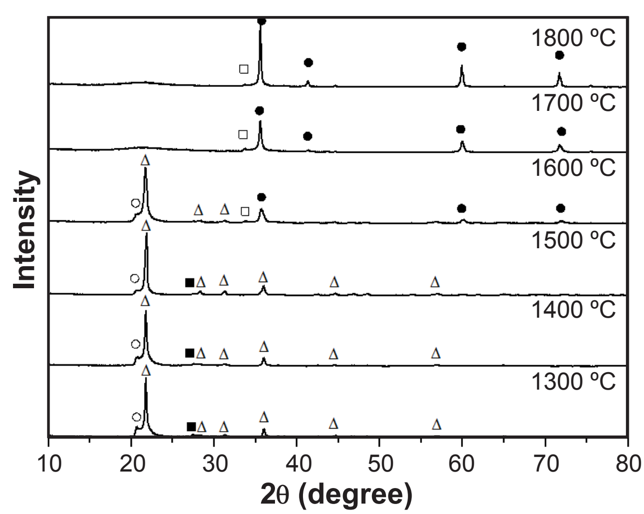

Figure 5: X-ray diffractograms of carbonized rice husk pyrolyzed at different temperatures for 2 h. Δ cristobalite; ○ tridymite; ■ quartz; • β-SiC; □ α-SiC.
[Figura 5: Difratogramas de raios X da casca de arroz carbonizada pirolisada em diferentes temperaturas por 2 h.]

Fig. 6 shows the concentration of SiC and SiO_2 in the final product as a function of pyrolysis temperature. As pyrolysis temperature increased, there was a higher SiC production and lower SiO_2 residue, mostly in the form of cristobalite. The same behavior was observed in [5, 6, 31]. SiC began to form at 1600 °C, and between 1700 and 1800 °C, only SiC was identified. Krishnarao and Godkhindi [5] studied a SiC production at lower temperatures, ranging from 1100 to 1510 °C; the maximum SiC concentration in the final product, about 58%, was obtained at 1510 °C. At 1500 °C, no SiC production was observed in the present study. In the production of SiC from a raw rice husk [31], it was observed that the production of graphitic carbon continuously increased up to 1600 °C. Graphite formation was not observed in the present study.

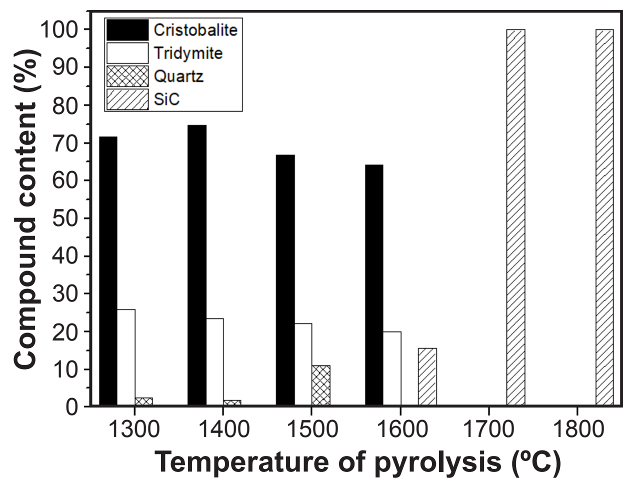

Figure 6: Comparison of SiC and SiO_2 production as a function of pyrolysis temperature.
[Figura 6: Comparativo da produção de SiC e SiO_2 em função da temperatura de pirólise.]

Fig. 7 shows SEM images of the pyrolyzed rice husk at 1500 °C (Figs. 7a and 7b), 1700 °C (Figs. 7c and 7d), and 1800 °C (Figs. 7e and 7f). At 1300, 1400, and 1500 °C, the presence of SiC was not observed, but only silica, mostly in the form of cristobalite. It was clearly observed that the SiC formed had two distinct morphologies: whiskers and particles. Between 1600 and 1700 °C, SiC formation was observed mostly in the form of whiskers. At 1800 °C, there was a decrease in whisker formation, and particulate SiC appeared. According to [5], when the pyrolysis temperature is increased, the formed filaments tend to recrystallize, and the product becomes predominant in particulate form. The SiC whisker formation seems to achieve a maximum in samples treated at 1700 °C. Krishnarao et al. [22] showed that there are competitive processes during the pyrolysis of rice husk: crystallization of amorphous silica, crystallization of amorphous carbon, and the reduction of SiO_2 to form SiC particles and whiskers. In the present study, the crystallization of the amorphous silica was observed at temperatures from 1300 to 1500 °C. Above 1500 °C, the reduction of SiO_2 to form SiC occurred. At 1700 °C, the rate of SiO liberation and the rate of SiC formation were probably low, favoring the formation of SiC whiskers. As the temperature increased, the rates of SiO release and SiC formation were probably high and favored the formation of SiC particles.

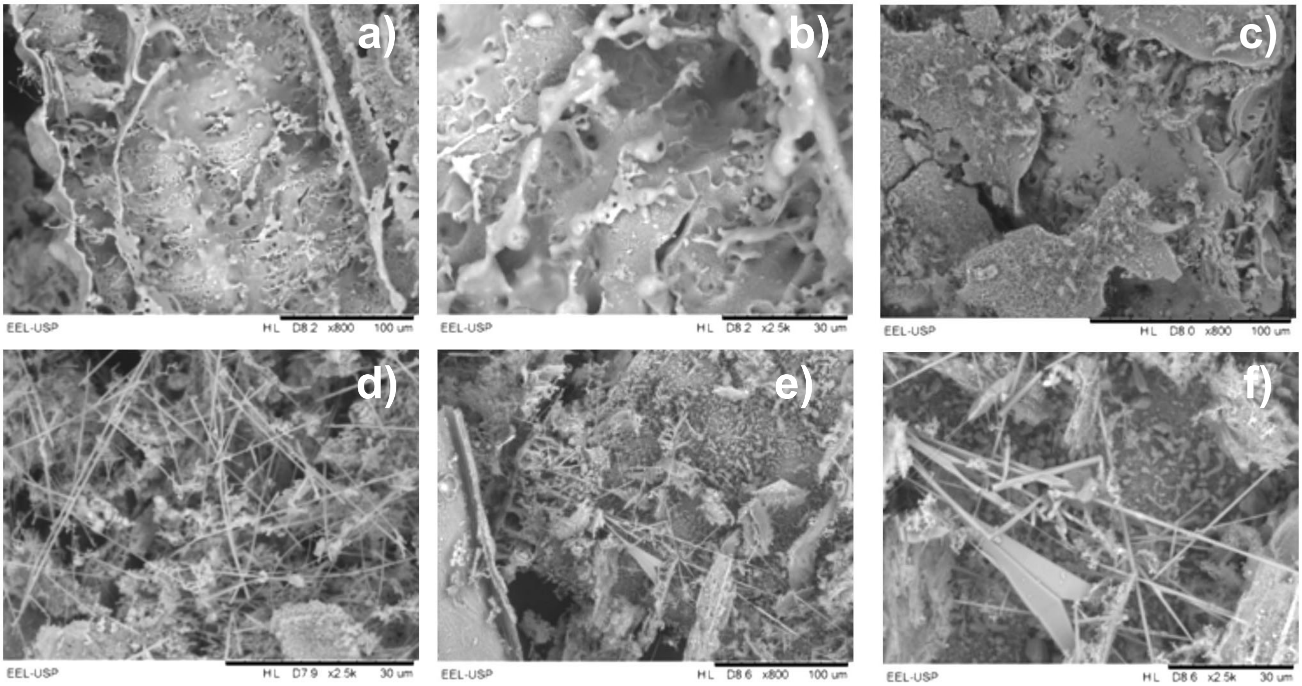

Figure 7: SEM micrographs of the pyrolyzed rice husk at 1500 °C (a,b), 1700 °C (c,d), and 1800 °C (e,f).
[Figura 7: Micrografias de MEV da casca de arroz pirolisada a 1500 °C (a,b), 1700 °C (c,d) e 1800 °C (e,f).]

CONCLUSIONS

SiC synthesis from rice husk was performed in a two-step process: carbonization and pyrolysis. It was concluded that pyrolysis temperature influenced SiC formation. SiC in whisker form was formed at 1600 and 1700 °C. At 1800 °C, there was a decrease in the whisker and particle formation of SiC; however, at 1700 and 1800 °C, only the SiC phase was identified by X-ray diffraction analysis; therefore, it was possible to obtain the SiC from rice husk. The SiC content in the final product from rice husk ranged from 15.7% to 100%, and the yield was 34.8% at 1700 °C and 29.9% at 1800 °C. Therefore, the use of rice husk in SiC production can bring several benefits beyond the environmental one; there could also be a reduction in the cost of the raw material since the rice husk is in most cases considered as waste and due to the intimate contact between silica and carbon, the rice husk has a high surface area which can lead to the formation of SiC at lower temperatures.

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