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Maximisation of SiC whisker yield during the pyrolysis of burnt rice husks

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Studies have been made on the conversion of burnt rice husks to SiC over a wide temperature range. Four distinct processes (crystallization of silica and carbon, formation of SiC whiskers and particles) have been identified as occurring during the pyrolysis of burnt rice husks. The dependence of relative rates of these four reactions on the temperature has been ascertained through detailed X-ray diffraction, scanning electron microscopy, chemical analysis and macro structural study. It was also revealed that a multistep pyrolysis to 1310 °C yields a higher SiC(w) than the single step pyrolysis. The yield of SiC(w) from burnt rice husks has been found to be lower than that from raw rice husks. A correlation between the amount of SiC(w) formed and the appearance of pyrolysed rice husks has been identified.

Introduction

Rice husks (RHs) are a unique agricultural waste product. RHs contain 15–20 wt % silica and a number of organic constituents, which will yield carbon when thermally decomposed [1]. There are several reports on the formation of SiC from rice husks [2–6]. In all the above cases the formation of SiC is accomplished in two steps. The RHs are coked in the absence of air at a temperature of 700–900 °C and then fired at temperatures (1500 °C) in an inert or reducing atmosphere.

Rice husks, as agricultural waste, have been used as a heat source for firing bricks and tiles in kilns, and for domestic heating. Large quantities of rice husk ash is available from the kilns of bricks and tiles. The ash obtained from RHs is of two types. White ash, relatively high in silica (>95% SiO_2), is obtained by complete burning of RHs. Black ash is obtained as a result of partial burning of RHs in the inner layers of rice husk heaps where they are not exposed to air directly. The RH black ash contains 40–55 wt % C. Because the carbon/silica ratio needed for the formation of silicon carbide, according to the following equation, should be 3:5, the RH black ash can be used for the formation of SiC

$$3C + SiO_2 \rightarrow SiC + 2CO \quad (1)$$

In an earlier study [7] it was observed that SiC(w) could also be produced from direct pyrolysis of rice husks and a step-heating of the charge in a graphite furnace under vacuum yielded a much higher percentage of SiC(w). The present investigation aimed to study the pyrolysis of burnt rice husks under vacuum conditions and to identify the parameters that tend to yield a high value of SiC whisker content.

2. Experimental procedure

The RHs used in the present investigation contain 15 wt % SiO_2 and 85 wt % C, and a negligible amount of other products.

The dry RHs were placed in a stainless steel dish. The RHs were ignited by inserting the dish and contents in a tube furnace at 700 °C and the RHs were allowed to burn. As soon as the flame disappeared the burnt RHs were quenched in air.

A sample of burnt RHs so obtained was taken in a 2.5 mm thick-walled cylindrical graphite crucible, closed with graphite lid. The graphite crucible was inserted into the heating zone of the graphite resistance heating furnace. An ASTRO high-temperature vacuum furnace model 1000A–2560, equipped with Honeywell small target radiation pyrometer model 939A3, was used for pyrolysis experiments. The furnace was connected to a HIND HIVAC vacuum system model VS-2 and a vacuum of the order of 5×10^{-2}–1×10^{-2} torr (6.67–1.33 Pa) was maintained during pyrolysis. Vacuum was released 8–10 h after the experiment was completed. The details of the experimental procedure have been described elsewhere [7].

Pyrolysis experiments were carried out at temperatures of 1100, 1150, 1200, 1250, 1310, 1410, 1510, 1610, and 1710 °C for 0.5 h. Experiments were also repeated for multistep pyrolysis by heating to a temperature of 1310 °C through a soaking for 15 min at 1150, 1200, 1250, and 1310 °C.

For the present study the techniques employed were X-ray diffraction (XRD), scanning electron microscopy (SEM) and chemical analysis. A Philips diffractometer model PW1840 with CuK_α radiation with a nickel filter was used. A Cam Scan DV-2 SEM was used to study the morphology of SiC. The excess

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carbon content was determined by burning at 700 °C for 3 h and the unreacted SiO_2 content was estimated by treating the carbon-eliminated sample with HF.

3. Results

The XRD patterns of the pyrolysed burnt RHs samples are shown in Fig. 1. The first appearance of the β-SiC peak was observed for a sample treated at 1150 °C. Simultaneously, a peak for crystalline silica also appeared. The peak at $2\theta = 22°$ corresponds to cristobalite. At temperatures below 1150 °C neither SiC nor crystallization of silica was detected. The percentage of SiC formed increased with increasing pyrolysis temperature. All peaks of β-SiC were observed for samples treated at or above 1410 °C. The degree of crystallization of silica reached a maximum at 1200 °C. The percentage of unreacted SiO_2 was reduced drastically in the samples treated above 1200 °C. The peak at $2\theta = 26°$ corresponds to graphitic carbon formed from the excess carbon in the samples treated at or above 1410 °C.

The appearance of heat-treated samples is shown in Fig. 2. There was no change in the appearance of sample after pyrolysis at 1100 °C, because no reaction was noticed. Formation of SiC particles and whiskers was observed from 1150 °C onwards. The samples were very fluffy and could not be tipped out of the crucible easily, after pyrolyses at 1150, 1200 and 1250 °C. As the pyrolysis temperature was increased

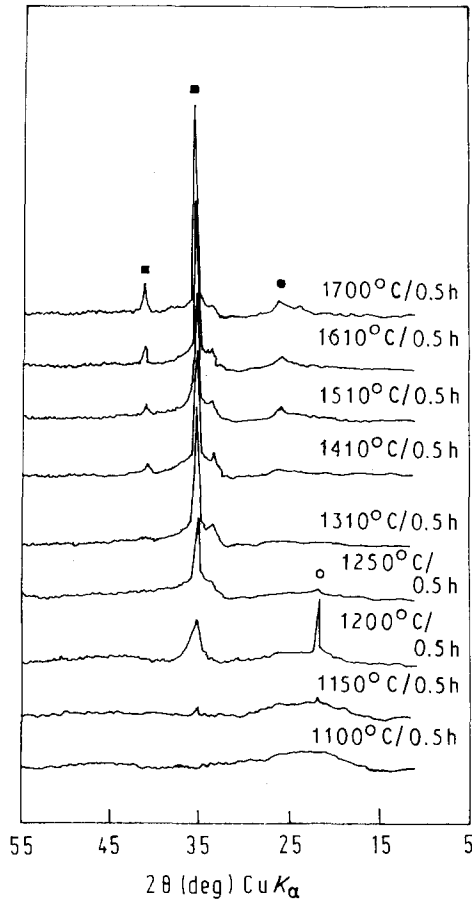


Figure 1 XRD patterns of pyrolysed burnt RHs. (○) Cristobalite, (●) graphite, (■) β-SiC.

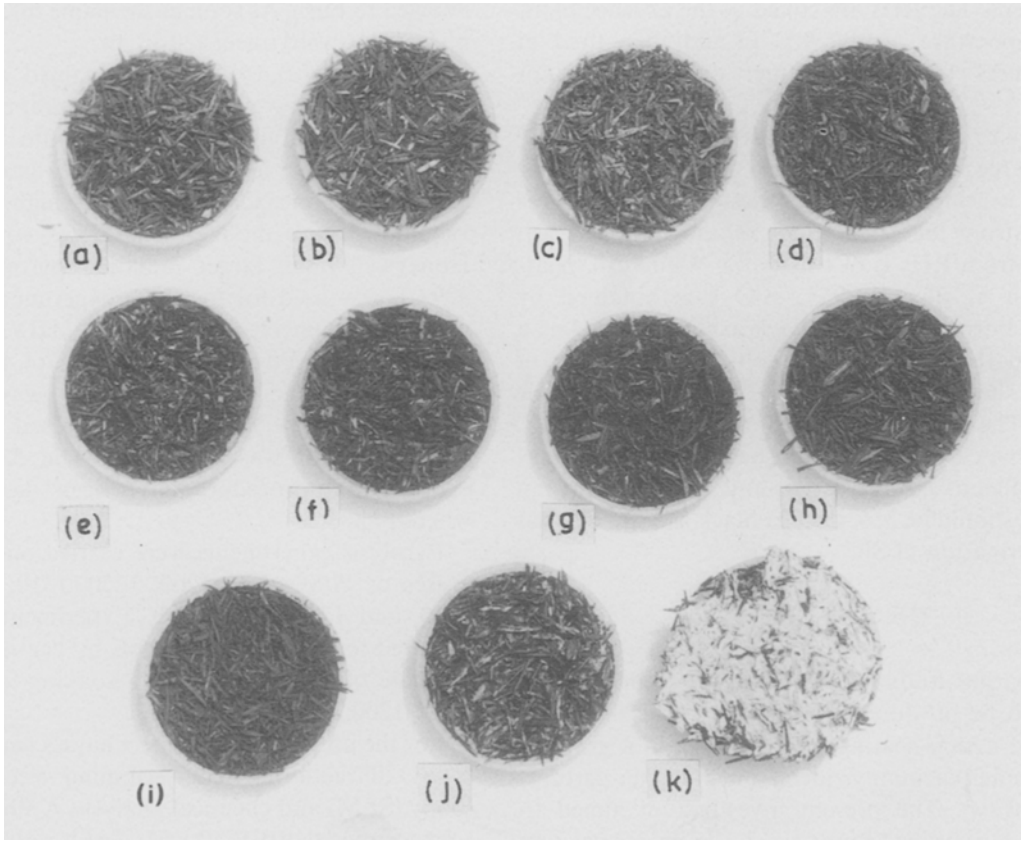


Figure 2 Appearance of burnt RHs after direct pyrolysis at (a) 1100 °C, (b) 1150 °C, (c) 1200 °C, (d) 1250 °C, (e) 1310 °C, (f) 1410 °C, (g) 1510 °C, (h) 1610 °C, (i) 1700 °C, (j) after multistep pyrolysis to 1310 °C, and (k) typical white deposition on top layers of pyrolysed RHs.

above 1310 °C, the samples contained loose particles. The samples appeared whitish after treatment at 1150, 1200 and 1250 °C, but this reduced from 1250 °C onwards, and turned to greenish at 1500 °C, 1600 °C and blackish at 1700 °C.

From SEM analysis of heat-treated samples, the formation of SiC particles and whiskers was detected at 1150 °C and above. The maximum quantity of SiC(w) was observed in the samples treated at 1200 °C (Fig. 3a). The coagulative recrystallization of SiC(w) was detected around 1310 °C. The progress of coagulative recrystallization of SiC(w) with increasing temperature is shown in Fig. 3b–d.

In an earlier investigation [7] it was observed that multistep pyrolysis of RHs favoured the formation of a greater quantity of SiC(w) than that formed by direct pyrolysis. In the present study, multistep pyrolysis was carried out by soaking the burnt RHs sample for 0.25 h at 1150, 1200, 1250 and 1310 °C. Both the quantity of SiC(w) formed and the whitish appearance of the sample after multistep pyrolysis (Fig. 2j) are higher than those of the sample directly pyrolysed to the same temperature (Fig. 2e).

A thick deposition on the top layers of the RHs and on inner surfaces of the crucible was observed after pyrolysis at 1150 °C and above. The colour of this deposition varied from whitish to greenish and blackish in a similar fashion to that observed in the appearance of bulk samples. This deposit is predominantly SiO_2 up to 1200 °C. As the temperature is increased, this deposition contained SiC whiskers and particles.

The burnt RHs used in the present study contained 46 wt % SiO_2 and 54 wt % C. When all the silicon in the black ash is converted to SiC, the sample after pyrolysis would contain 52.73 % SiC and 46.26 % excess carbon. The variation in the percentage of excess carbon and unreacted SiO_2 in the heat-treated samples is shown in Fig. 4. The percentage of SiC formed increased steeply from 1150–1410 °C. At 1510 °C the quantity of SiC formed is −90 % theoretical value and above 1510 °C increased only slightly. Even at 1700 °C, about 4 wt % unreacted SiO_2 was detected. This shows that the SiO_2 reduction process does not proceed to completion even at 1700 °C.

4. Discussion

The results of the present study show that there are four competitive processes occurring during the pyrolysis of burnt RHs. They are the crystallization of amorphous silica, the crystallization of amorphous carbon, and the reduction of SiO_2 to form SiC particles and whiskers. The crystallization of amorphous silica is accelerated with increase in temperature from 1100–1200 °C. At and above 1250 °C the reduction of SiO_2 to form SiC becomes rapid. The percentage of SiC formed increases on increasing the temperature from 1150 °C. The maximum percentage of SiC(w) formation was observed at 1200 °C (Fig. 2c) where crystallization of silica and its conversion to SiC are two dominant processes (Fig. 1c). The rate of release of SiO and the rate of SiC formation are probably low enough for the perferred formation of SiC whiskers at 1200 °C. Above 1250 °C, the rate of release of SiO and the rate of SiC formation are probably high, and favour the formation of isometric SiC patrticles. From

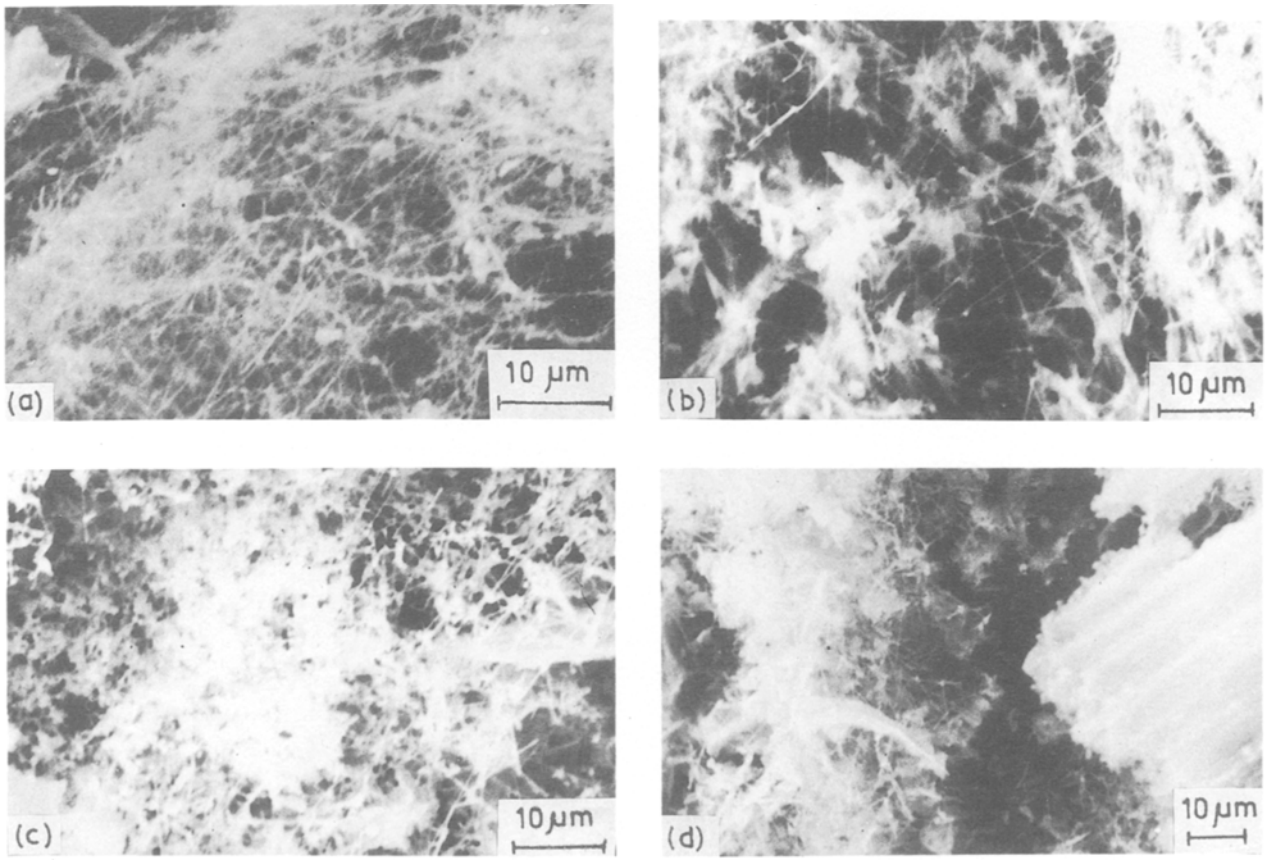


Figure 3 Progress of coagulative recrystallization of SiC(w) at (a) 1200 °C, (b) 1310 °C, (c) 1410 °C, and (d) 1510 °C.

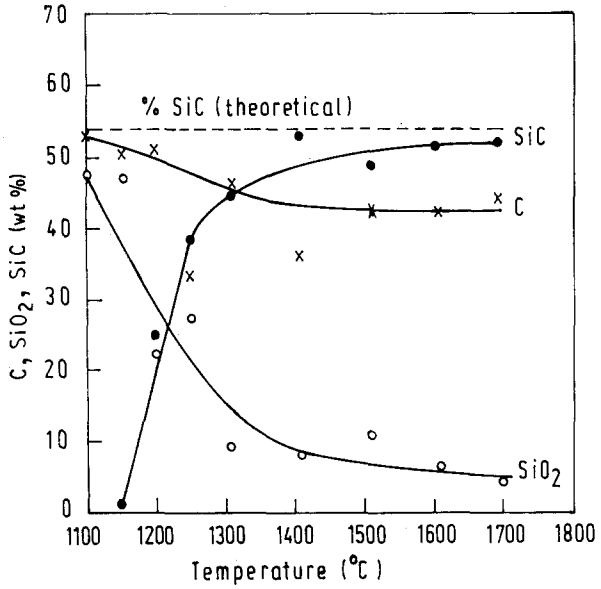
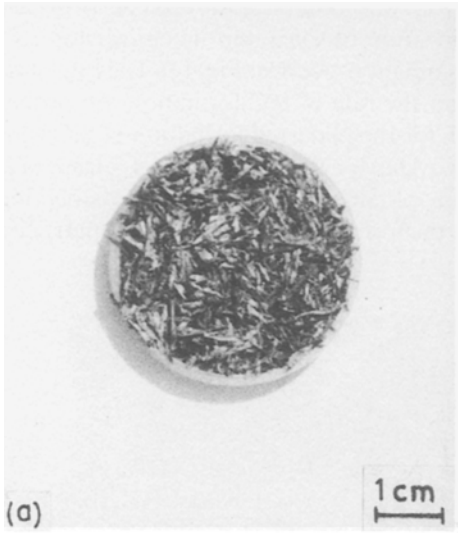


Figure 4 Variation of the percentage of C, SiO_2 and SiC after pyrolysis as a function of temperature.



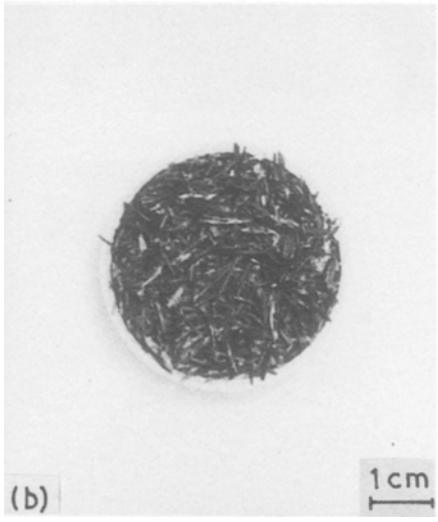


Figure 5 The appearance after multistep pyrolysis to 1310 °C of (a) raw RHs, (b) burnt RHs.

1310 °C, the degree of recrystallization of SiC(w) increases with increasing temperature. Above 1510 °C, the SiC formed consists predominantly of isometric particles. The graphitization of excess amorphous carbon is favoured above 1410 °C.

During the multistep pyrolysis, as the sample was soaked for 0.25 h at each temperature (1150, 1200, 1250 and 1310 °C), the silica tended to crystallize and indirectly favoured the formation of a large quantity of SiC(w). The low rate of SiC formation due to the conversion to crystalline silica and the controlled release of SiO at each of the temperatures, are probable reasons for the increase in the quantity of SiC(w) formed. It was been shown in our earlier investigation [7] that a rough estimation of the percentage of SiC(w) formed in RHs can be made from SEM analysis and the whitish appearance of heat-treated RHs. However, the quantity of SiC(w) formed in burnt RHs (Fig. 5b) is much lower than that formed from raw RHs (Fig. 5a).

The above results show that SiC can be produced from RHs after utilizing their heat energy. The RHs black ash available from brick kilns, etc. could be used for the production of SiC. By choosing the appropriate pyrolysis temperatures, the formation of two types of SiC (particles and whiskers) can be controlled.

5. Conclusions

1. Conversion of amorphous silica to cristobalite, formation of SiC whiskers and polycrystals, and graphitization of amorphous carbon have been identified as four reactions occurring during the pyrolysis of burnt rice husks in vacuum.

2. While the total percentage of SiC formed increases as a function of temperature, the conversion to SiC whiskers seems to attain a maximum around 1200–1250 °C.

3. A multistep heating to 1310 °C is found to yield much higher amounts of SiC(w) than a single step pyrolysis.

4. The formation of SiC(w) in burnt RHs is found to be lower than that in raw RHs.

5. The relative amounts of SiC(w) formed from RHs can be estimated from SEM analysis and the visual appearance of pyrolysed RHs.

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