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Effect of catalyst and process parameters on the production of silicon carbide from rice hulls

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Abstract

Several routes for the production of SiC by pyrolysis of rice hulls have been examined. Under reducing and proper reaction conditions, four distinct processes have been identified; these are, decomposition of silica and cellulose and the formation of SiC particles and whiskers. The effectiveness of sodium silicate as a catalyst on maximisation of SiC yield has been discussed. The dependence of SiC yield on the pyrolysis temperature and atmosphere has been described. The reaction products were investigated by XRD, EDS, and SEM. Optimum conditions for the highest SiC yield were determined, and mechanisms for the nucleation and growth of SiC whiskers were discussed.

1. Introduction

The potential feature of rice hulls is their high silica content (15–20 wt%) with small amount of alkalis and trace elements [1,2]. Silica is distributed in the backbone cellulose structure of the rice husk, such that its content is more in the exterior compared with the inner walls [2,3]. Heating the husks produces amorphous carbon as the by-product of carbonisation of cellulose, while silica remains unchanged. Pyrolysis of the ash at high temperatures and under controlled atmosphere promotes carbothermal reduction of silica and formation of SiC.

Synthesis of SiC from rice husks was initiated by Culter and Lee in 1975 [4]. Several other researchers attempted various alternative routes to characterise the formation of SiC during carbothermal processes [5–10]. Accordingly, three reactions are responsible for the SiC formation at temperatures from 1200 to 2000°C. These are:

$$SiO_2 + 3C \rightarrow SiC + 2CO$$

$$SiO_2 + 2C \rightarrow Si + 2CO$$

$$SiO_2 + C \rightarrow SiO_{(g)} + CO_{(g)}$$

These reactions take place as competing processes at different temperatures and pressures. The same reactions occur at higher temperatures between solid quartz and graphite. In the rice husks with the very high surface area and close contact between the amorphous silica and carbon, SiC forms at lower temperatures (1200-1500). Another advantage of the low temperature formation of SiC is the lack of agglomeration and bonding of particles. Fine SiC particles and whiskers are produced, and can be separated easily. All the past attempts can be classified into three groups, namely: two step, single step, and multistep pyrolysis of the rice husk. The two step method, the oldest one, consists of heating the husks at approximately 900°C for two h followed by vacuum pyrolysis at 1500°C [4]. The single step method was a direct pyrolysis carried out at about 1300°C under inert gas or vacuum [8].

In the multistep method, heating was carried out at several temperature intervals for 15 min. An advantage of the multistep pyrolysis was enhancement of whisker formation compared to other methods [8].

Effects of prewash, chemical treatment, and catalysts on the formation of SiC have been the focus of some other works [2,4,6]. Acid wash in HF, NaOH and NH_4OH caused liberation of silica in the husk [3].

In the present work, effects of sodium silicate, Na_2SiO_3, as a catalyst on the maximisation of SiC whiskers was investigated. Sodium silicate was chosen for its low melting point and presence of amorphous silica. Single step pyrolysis at a low temperature range of 1100–1400°C under inert gas media proved to be very effective. Analytical instruments were exploited to

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characterise the reaction products, and the mechanism of SiC nucleation and growth was discussed.

2. Experimental procedures

The dry rice husks were selectively chosen to eliminate impurities. The water content was measured to be about 9.6 wt% which could be removed by heating at 150°C for about 30 min. Heating to 300°C released some other organics containing hydrogen, oxygen, nitrogen and carbon. Carbon content was measured by a C-Mat instrument to be 40 wt%. In this instrument, the carbonaceous portion of the husk is burnt and converted to CO_2 which could be detected. It should be noted that not all carbon content of the husk is convertible to amorphous carbon and eventually to SiC, but part of it leaves the husk with volatile species upon heating.

Silica content of the husk was measured by atomic absorption spectroscopy and by gravimetric methods as advised by Vogel [11]. The results are given in Table 1. The 17.1% silica ranks the used husks as an average grade type.

Rice hulls were washed in deionized water and were dried at 80°C in a hot oven. They were placed in a graphite crucible, with a porous lid to let out gassing while argon flows inward. Controlled atmosphere was important. High argon flow reduces SiO pressure and low gas flow leaves CO in the pyrolysis chamber, both of which decelerate reactions and reduce SiC yield. Effects of air and argon atmosphere were reported earlier [10]. Single step, two step and multistep pyrolysis of the rice husks were performed. In single step method, the raw hulls were pyrolysed directly at temperatures from 1200 to 1400°C and in 1/2 to 3 h. In the two step process, hulls were burned at 700°C up to the point when glowing diminished, and the ash was pyrolysed at a secondary high temperature. In multistep process, the raw husks were pyrolysed at a sequence of 1150-1200-1250-1300-1350°C at a heating rate of 50°C min^{-1}, holding 15 min at each temperature.

To study effects of catalyst, husks were soaked in sodium silicate solution to ensure uniform coatings, then were dried and pyrolysed. Concentration of the solution (1–10 gl^{-1}) and soaking time (up to 12 h) were shown to be crucial for maximisation of the SiC yield. Products of the pyrolysis were SiC whiskers and particles, carbon and unreacted silica. Heating at 700°C for

Table 1
wt% of silica in the rice husk

Method	%Si	%SiO_2
Atomic Absorption	7.9	17
Gravimetry	8.03	17.19
Average	7.96	17.1

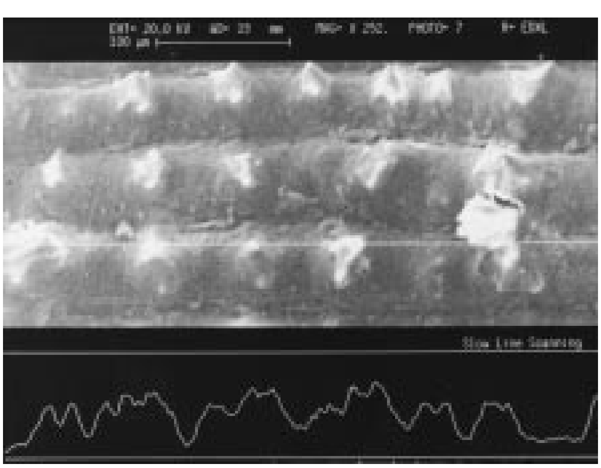

Fig. 1. Outer surface of the rice husk with its Si X-ray line scan.

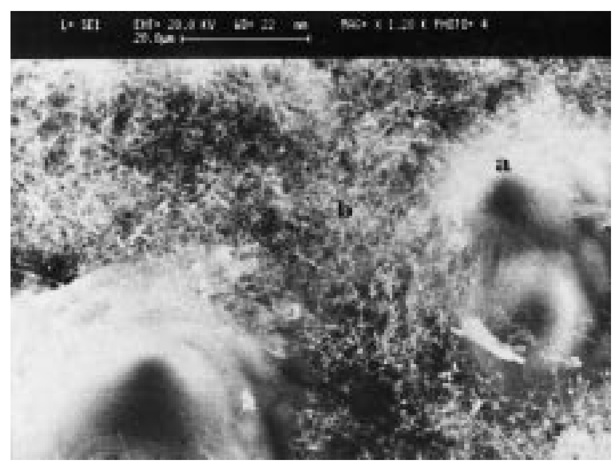

Fig. 2. Products of the 1350°C pyrolysis, SiC particles and whiskers, pictured on the outer surface of the husk: (a) at summits (b) at grooves.

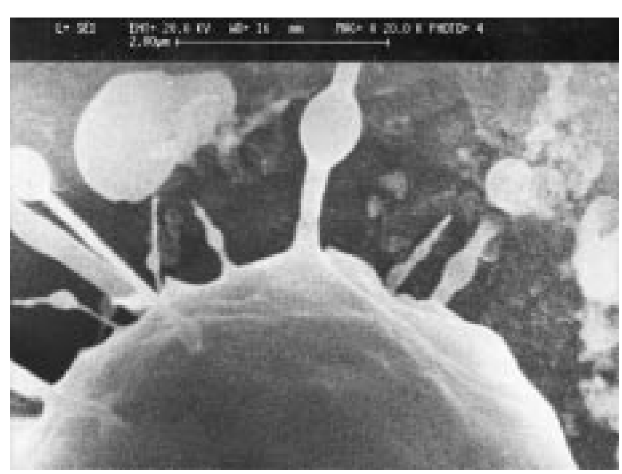

Fig. 3. Whisker formation at the sites containing impurities.

3 h in air removed residual carbon, and soaking in HF removed any unreacted silica or surface oxides. SiC whiskers were separated from SiC particles and other carbonaceous residue by selective and immisible liquid separation techniques [12]. Analytical instruments were exploited for characterisation of the constituents, phases and microstructures at different stages of the experiments.

3. Results and discussion

The SEM picture of the outer surface of the dry rice husk with the Si X-ray line scan is shown in Fig. 1. One can see that silica content is higher at the peaks, compared to its value at the grooves on the surface. This could be due to the presence of free silica at the peaks and bond silica-cellulose in the grooves [3]. After pyrolysis, SiC particles and whiskers were formed more intensely at the grooves (Fig. 2). A comparison of Figs. 1 and 2 suggest that Si from the peak areas diffused via a gas phase to combine with the cellulose containing carbon at the valleys to form SiC. A higher magnification of the as-pyrolysed products is shown in Fig. 3. Whiskers were nucleated at preferential sites containing trace impurities (K, Ca, Mn,..) and grew outward. EDS results of different parts of a whisker are

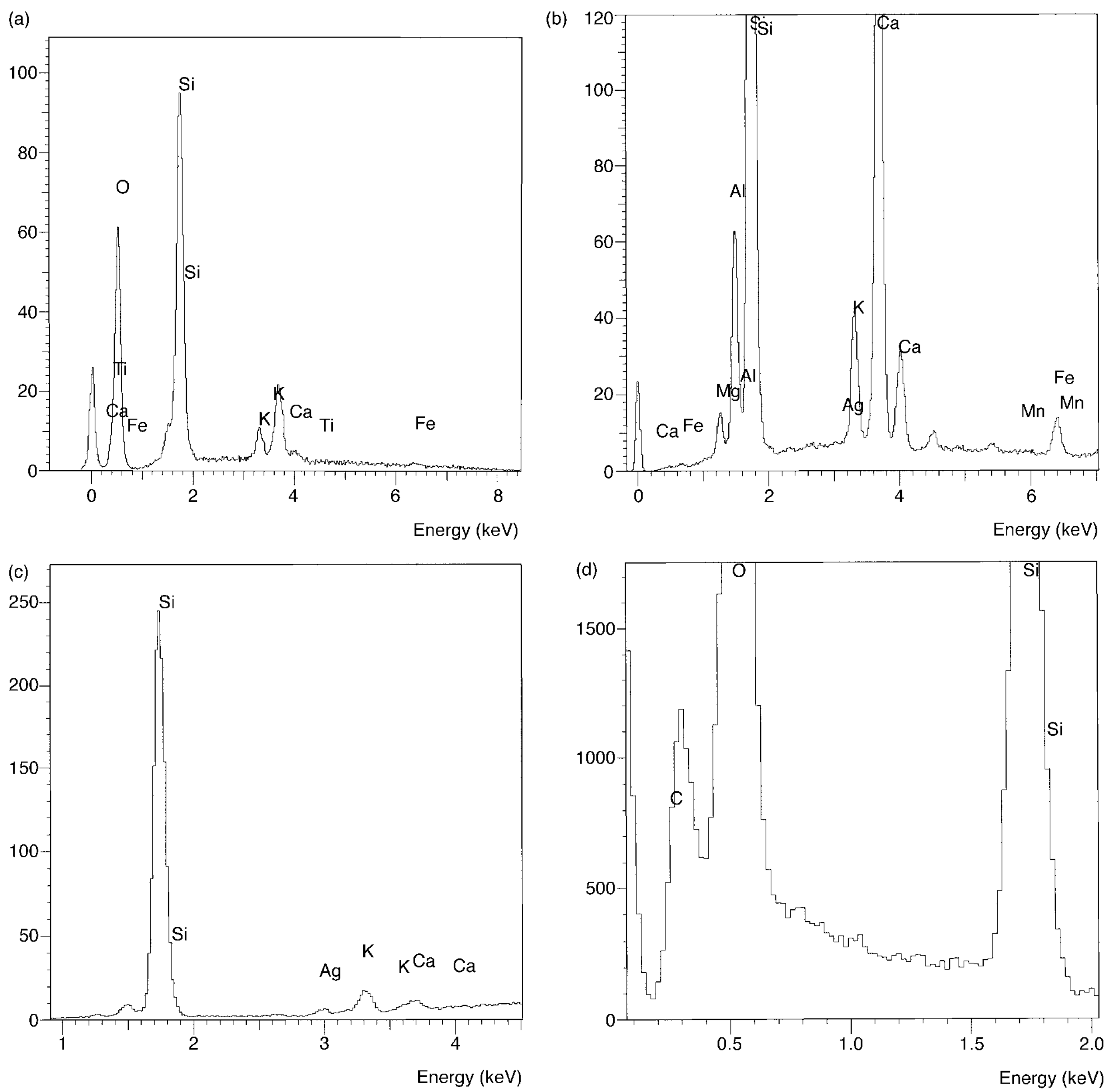

Fig. 4. EDS X-ray K_{α} lines: (a) taken at the nucleation sites of the whiskers; (b) taken at a bulb on the whiskers; (c) at a flat section of a whisker; (d) same as (c) but measured with windowless detector, showing C and O X-ray peaks.

shown in Fig. 4;4(a) taken at the nucleation site of the whiskers in Figs. 3 and 4(b) at a bulb on the whisker, and 4(c) at a flat section.

Fig. 4(d) was taken at a flat section of a whisker using windowless EDS detector, so oxygen and carbon peaks are visible. The oxygen peak is an indication of the surface oxide film which could be removed by HF wash.

SiC particles and whiskers after seperation are shown in Fig. 5. Whiskers have different morphologies including cylindrical, branched and knotty.

X-ray diffraction using CuK_{α} radiation was performed on most of the pyrolysed products. Results for single step pyrolysed husks at 1350°C are shown in Fig. 6. The prominent peak at $2\theta = 35.8°$ belongs to (111) planes of β-SiC (cubic form of SiC) which shows an increase at 1350°C (other peaks appear at 41.2°, 59.6° and 71.5°). The remaining peaks belong to graphite ($2\theta =$ 26.6°) and crystobalite (SiO_2, $2\theta = 21.90°$).

Effects of sodium silicate soaking is demonstrated in Fig. 7. A comparison of Figs. 6 and 7 concludes the positive catalyst effect of sodium silicate. Best SiC yield was obtained at a sodium silicate concentration of 1 gl^{-1}. Higher concentration to 10 gl^{-1} caused a thick coating on the rice husk and consequently decreased the pyrolysis reactions.

To characterise effects of temperature and time on the SiC yield, weight fraction of the pyrolysis products under different conditions were determined after being separated. Here, results of single step pyrolysis under argon atmosphere will be discussed.

Fig. 8 depicts wt% of the products vs temperature. It shows that 1200°C is almost the minimum temperature of the pyrolysis; the higher the temperature, the higher is the SiC yield. The horizontal dash line at 58.3% shows the theoretical limit for SiC yield, assuming that all the silica in the raw rice husk were converted to SiC without any residue unreacted silica. Effect of time on the SiC yield is shown in Fig. 9 showing a decreasing rate, approaching the theoretical value of 58.3% at 1350°C and 4 h.

Concentration of sodium silicate and its effect on the wt% of SiC, SiO_2 and C is depicted in Fig. 10 The optimum condition was obtained at a concentration of 1 gl^{-1} of Na_2SiO_3 and at 1400°C for the total SiC (Fig. 11). A comparison of Fig. 8 with Fig. 11 is worth noting, and is depicted in Fig. 12. The efficiency of the

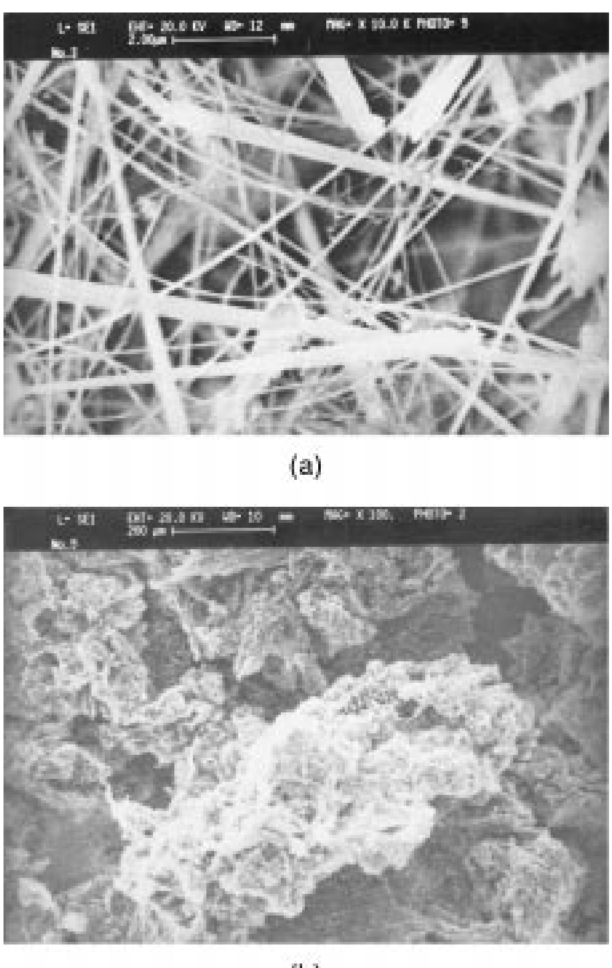

Fig. 5. (a) SiC whiskers and (b) particles after separation.

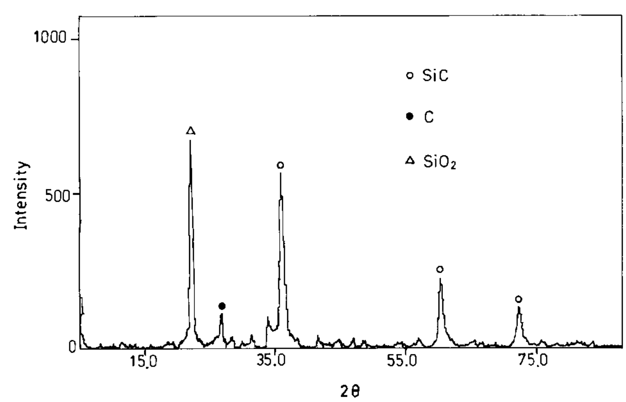

Fig. 6. XRD patterns of the pyrolysed products at 1350°C.

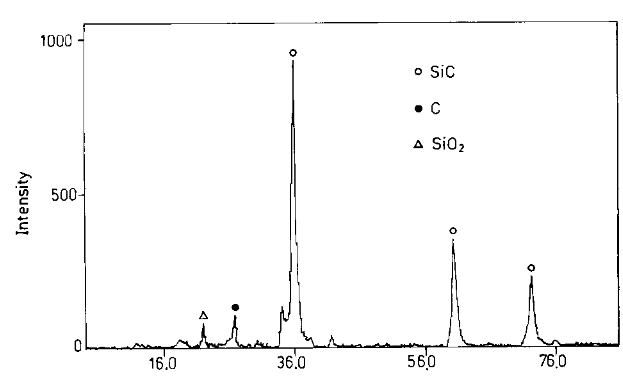

Fig. 7. XRD patterns of the products at 1350°C, husks were soaked in sodium silicate prior to pyrolysis.

conversion of silica to SiC was promoted by soaking in a dilute concentration of sodium silicate. According to Nutt [13], and based on our observations (Figs. 3, 4(a) and (b)), impurities such as Ca, K, Mn and complex silicates facilitate nucleation of whiskers. Sodium silicate (Na_2O, SiO_2, nH_2O) has a low melting point (800–900°C) and forms a glassy silicate coating on the husks. A low concentration of Na_2SiO_3 produces a dispersed silicate on the husk which act as sites for nucleation of SiC whiskers. Higher concentration of Na_2SiO_3 produces thicker coating on the husk surface, though promotes SiO_2 formation, but causes a barrier between the SiO gas in the media and the amorphous carbon in the husk, and delays the pyrolysis reactions.

Increasing temperature above 1350°C, increased the rate of reaction and wt% of total SiC, but decreased wt% of SiC whiskers. Higher temperature caused sintering of SiC powders. This was also observed by Krishnarao et al. [8]

Results of multistep pyrolysis showed a lower total wt% SiC, compared to the direct pyrolysis, both with and without sodium silicate soaking. For example 40.1 wt% in multistep compared to 50.6 wt% in the direct pyrolysis at 1350°C. This was due to lower

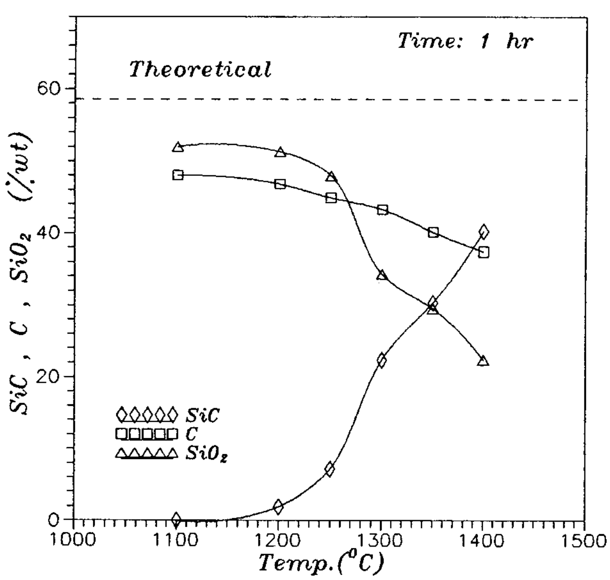

Fig. 8. Effect of pyrolysis temperature on the SiC yield of the product.

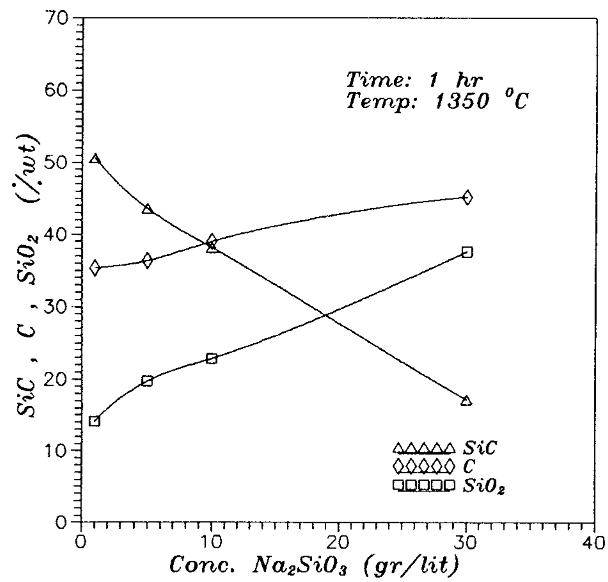

Fig. 10. Effect of the concentration of the sodium silicate on the product yield after pyrolysis at 1350°C for 1 h.

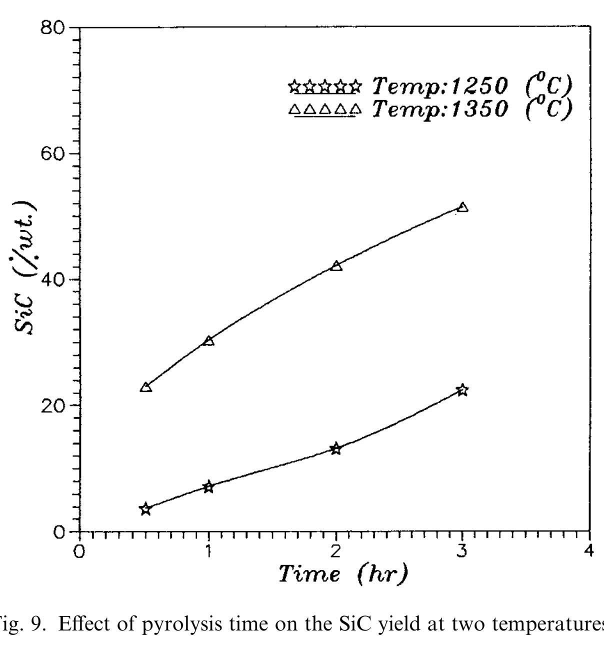

Fig. 9. Effect of pyrolysis time on the SiC yield at two temperatures.

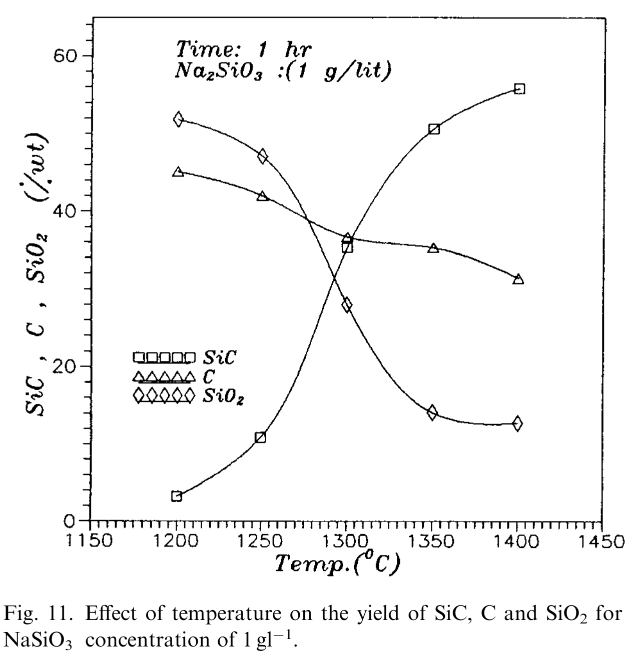

Fig. 11. Effect of temperature on the yield of SiC, C and SiO_2 for a $NaSiO_3$ concentration of 1 gl^{-1}.

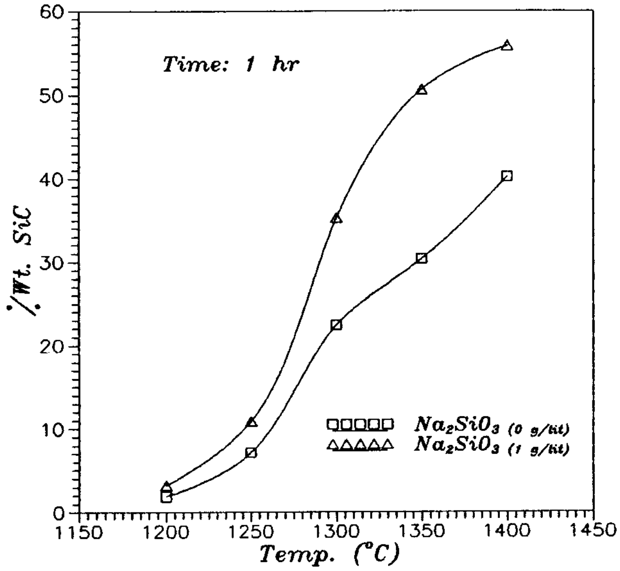

Fig. 12. Catalytic effect of Na_2SiO_3 on the SiC yield at all test temperatures.

holding times at higher temperatures and presence of unreacted silica in the pyrolysis products. Krishnarao et al. [8] reported a higher SiC whisker yield under multistep pyrolysis done under vacuum. A rapid glance at the vacuum and multistep process and equipments used by others [8] and the inert gas process and catalyst used in this work suggests that the latter is more cost effective and achievable.

4. Conclusion

The rice hulls used in the present work contained 17% silica which theoretically could produce a maximum of 58.5 wt% SiC. Direct pyrolysis at 1400°C and 3 h, under flow of argon, without catalyst (Na_2SiO_3) and/or at 1400°C and 1 h with catalyst resulted in a near maximum yield of SiC whiskers and particles. Whiskers had several morphologies and were 0.1–1 μm thick and 10–50 μm long. Multistep pyrolysis to 1350°C reduced total SiC, while a slight increase in the SiC whiskers was noticeable. Soaking in dilute solution of sodium silicate enhanced the formation of SiC whiskers and particles; a higher yield was achieved in a shorter time. Concentration of the catalyst and soaking time are crucial parameters for maximization of the SiC yield.

Acknowledgements

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