Pyrolysis of rice husk

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Rice husk has proved to be a difficult fuel for gasification and fluidized bed combustion because of the high ash content resulting in carbon conversion inefficiency. We report the results of pyrolysis experiments of individual rice husk particles under controlled atmospheres of the confocal scanning laser microscope followed by SEM observations of the pyrolized structure of the particles. The results suggest a preferential shrinkage of the particles in the transverse direction, implying the presence of strong and inert silica layer that retains its structure despite high temperatures. The cellulose and lignin component was preferentially consumed in geometrically arranged pores and channels. The role of silica appears to be more than just a geometric shield and thus complete carbon conversion may not be achievable.

RICE husk is the outer covering of paddy and accounts for 20–25% of its weight[1]. It is removed during rice milling and is used mainly as fuel for heating in Indian homes and industries. Its heating value of 13–15 MJ/kg[1,2] is lower than most woody biomass fuels. However, it is extensively used in rural India because of its widespread availability and relatively low cost. The annual generation of rice husk in India is 18–22 million tons[3] and this corresponds to a power generation potential of 1200 MW[4]. A few rice husk-based power plants with capacities between 1 and 10 MW are already in operation and these are based either on direct combustion or through fluidized bed combustion. Both these routes are beset with technical problems because of the chemical composition of rice husk and its combustion characteristics[2].

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Rice husk is characterized by low bulk density and high ash content (18–22% by weight). The large amount of ash generated during combustion has to be continuously removed for a smooth operation of the system. Frequently, the throat of downdraft gasifier gets clogged because of the sintering (caking) of the ash generated in the gasifier[5]. The rice husk gasifier virtually acts as a pyrolyzer since the residence time for the particles is often not long enough for char gasification reactions to proceed[6]. This results in poor carbon conversion efficiency[7,8], sometimes as low as 55%. It has also been reported that the main reason for a poor utilization of carbon is due to difficulties in accessing all the carbon present in the material. Some of it, trapped as chemical compounds in the ash, is not easily gasified or burnt[2].

Silicon oxide forms the main component (90–97%) of the ash with trace amounts[2,7] of CaO, MgO, K_2O and Na_2O. The melting point of SiO_2 is 1410–1610°C, while that of K_2O and Na_2O is 350 and 1275°C respectively[7]. It has been suggested that at higher temperatures, the low-melting oxides fuse with silica on the surface of the rice husk char and form glassy or amorphous phases, preventing the completion of reaction[9]. This places an upper limit on local temperature of the gasifier[10]. Similar behaviour was also observed in fluidized beds where the bed materials, sand or alumina react with rice husk particles forming soft agglomerates and preventing the completion of pyrolysis and combustion reactions.

Most of these observations were from bulk studies on rice husk and pyrolyzed products from gasifiers, as it was not possible to conduct *in situ* investigations on the pyrolysis of individual particles under controlled heating and atmospheric conditions. The experimental difficulties in carrying out such studies have now been overcome with the availability of confocal scanning laser microscope (CSLM) with appropriate environmental chambers. In the following sections, we describe the results of pyrolysis and combustion experiments carried out on individual rice husk particles under controlled conditions in an environmental chamber attached to the CSLM. The results from these experiments were supplemented by SEM observations of the rice husk structure before and after pyrolysis.

CSLM combines the advantages of confocal optics with a He-Ne laser, thereby enabling observations of samples at high resolution and at elevated temperatures. The confocal optics enables the detection of strong signals from objects on the focal plane with weak ones from those not on that plane. By scanning a surface at various focal depths, a 3D image is constructed that faithfully records uneven surfaces. The utilization of a laser results in high illumination intensity that overcomes the noise generated by the thermal radiation present in materials at elevated temperatures. The optical set-up of this system thus has an improved signal-to-noise ratio, better contrast between different phases and higher resolution. For instance, this microscope is capable of resolving features down to fractions of micrometres under controlled thermal fields and atmospheres, and can be operated up to 1700°C. Although confocal microscopy has been used quite extensively in biological research[11], it is only recently that the laser integrated microscope with high temperature capabilities has entered into materials research. The CSLM at Carnegie Mellon, the only one of its kind in the US, is shown in Figure 1.

Pulverized and sieved rice husk samples with sizes in the range between 250 and 300 μm were chosen for the experiments. The particles were roughly cylindrical with large aspect ratios. A single particle was placed in a crucible inside the furnace of the CSLM and was heated at a rate of 50°C/min in an inert atmosphere of flowing argon gas. The heating was mainly by radiation and the convection effects were negligible. Argon was purified by passing through a Cu-Mg heating coil. As a result, the oxygen partial pressure in the gas was reduced to 10^{-12} atm. The real-time visual images of the particle were recorded in a monitor, and still frames were later selected to analyse the particle shape and size as a function of temperature and time. This procedure was repeated for 20 randomly chosen particles of different shapes. Figure 2 shows the images of the same particle at different temperatures: 155, 432, 710 and 810°C.

The above micro-structural observations show that there is virtually no change in size or shape of the particle until ~ 200°C. This is followed by a rapid shrinkage between 200 and 400°C. Above 400°C, the particle shrinks at a slow rate and stops shrinking after ~ 800°C. Two distinct stages in the shrinkage of particles are clearly seen (Figure 3 *a*), when the effective radius of the particles is plotted as a function of temperature. Mansaray and Ghaly[12] reported a similar two-stage weight loss in thermo gravimetric experiments for different heating rates and atmospheres. The first stage can be explained as due to a rapid thermal degradation due to volatiles escaping from the particle. This process is complete when the temperature rises to ~ 400°C. The second stage is because of char combustion due to oxygen (present in argon) and gases generated from

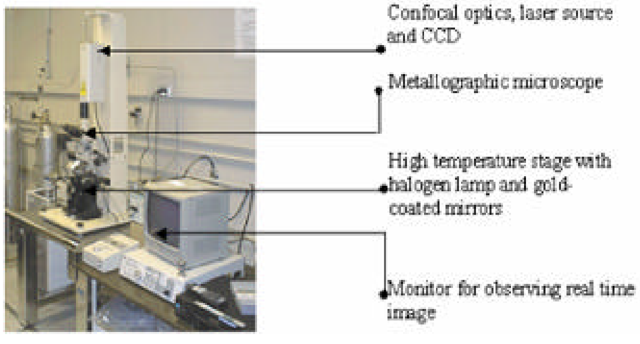

Figure 1. Confocal scanning laser microscope at Carnegie Mellon University.

the first stage. This stage is sluggish and less pronounced in rice husk.

An important feature of this shrinkage is that the size reduction along the transverse direction of the largely longitudinal husks was significantly larger than along the longitudinal axis. Circumscribing an ellipse around the particle and calculating the aspect ratio captures this effect. In Figure 3 *b*, the aspect ratio (*L*/*D*) increased from an initial value of 2.19 to 3.23.

Figure 4 *a* and *b* shows the experimental results obtained for several particles of different initial shapes and sizes examined in the study, but with a heating rate of 200°C/min. The trends are similar to the ones described above. The two-stage mechanism for particle shrinkage is

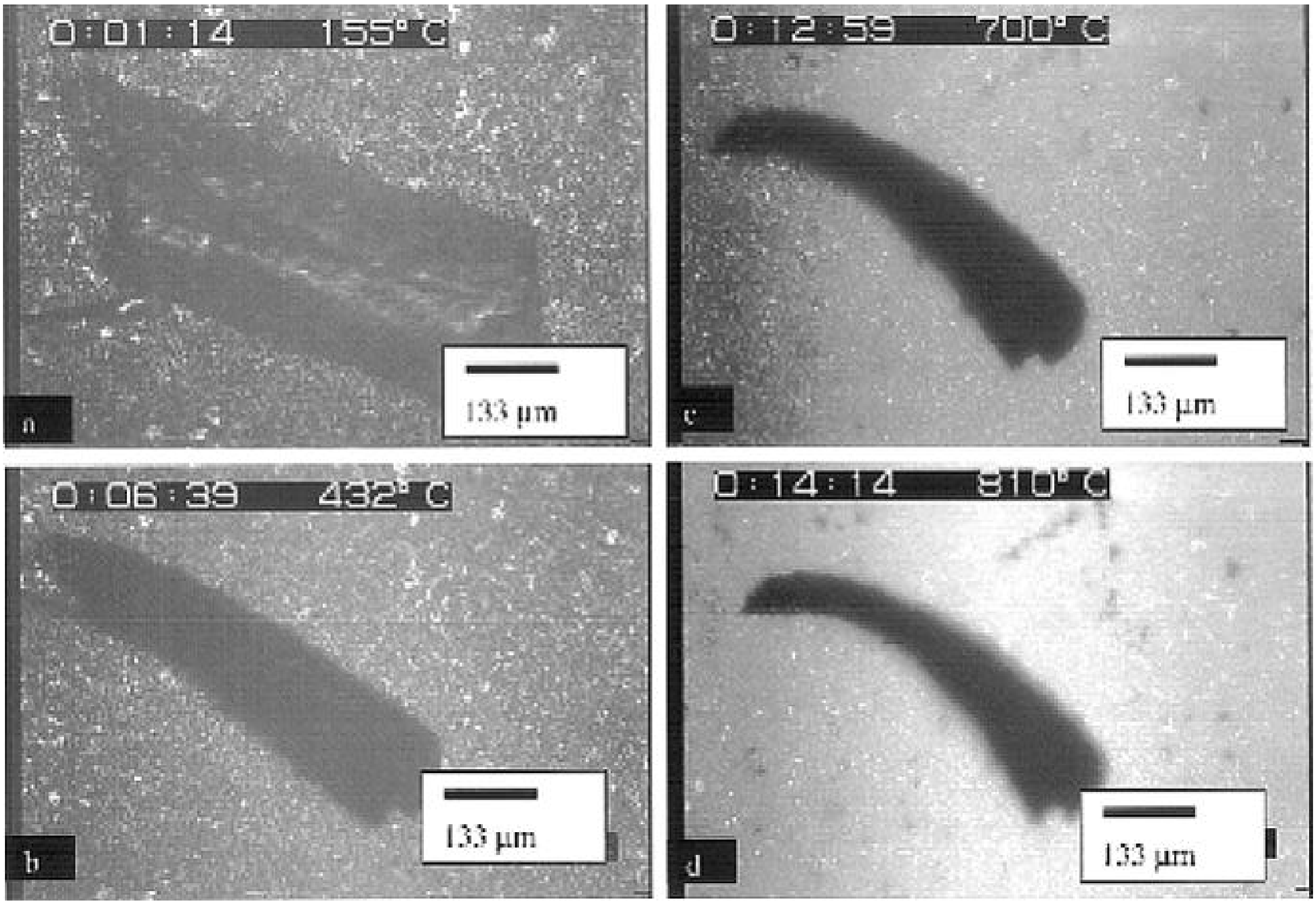

Figure 2. CSLM images of a rice husk particle heated in flowing argon at various temperatures. Particle shrinkage is much more in the transverse direction than in the longitudinal direction.

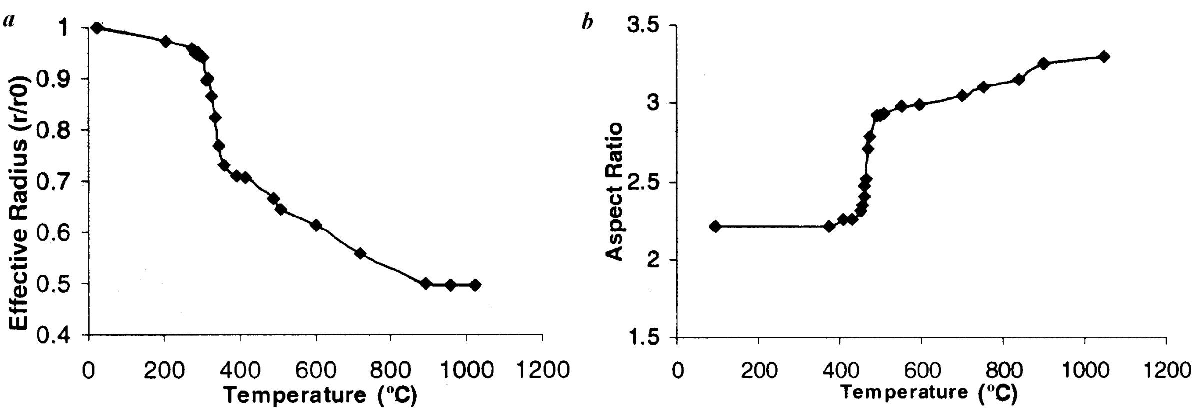

Figure 3. *a*, Effective radius of particle shown in Figure 2. *b*, Aspect ratio of particle vs temperature.

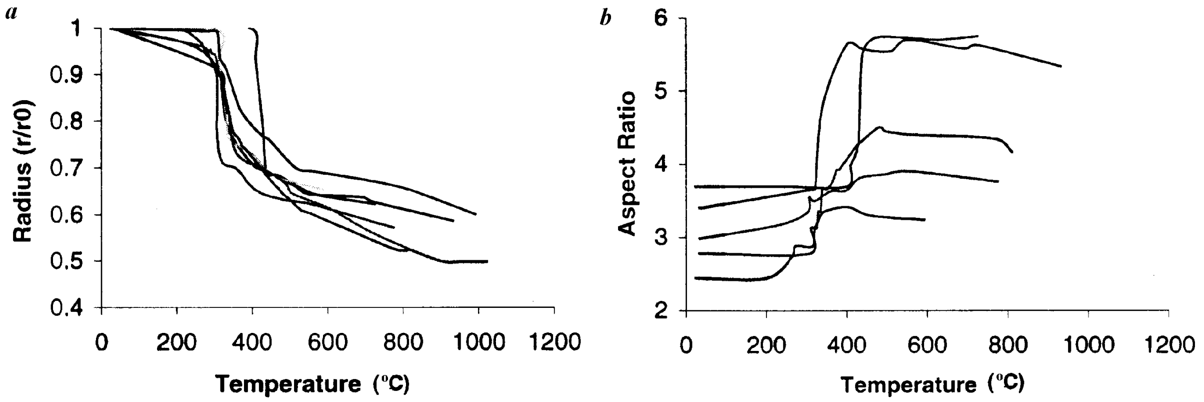

Figure 4. Effective radius (***a***), and aspect ratios (***b***), of different particles at a heating rate of 200°C/min in flowing argon with an oxygen partial pressure of 10^{-12} atm.

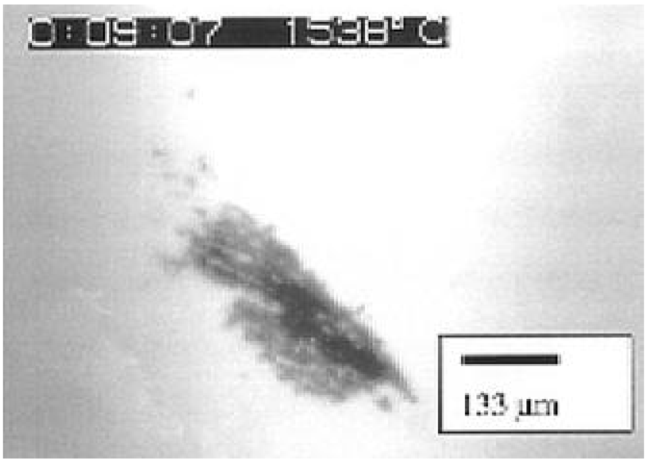

Figure 5. Softening and melting of rice husk sample.

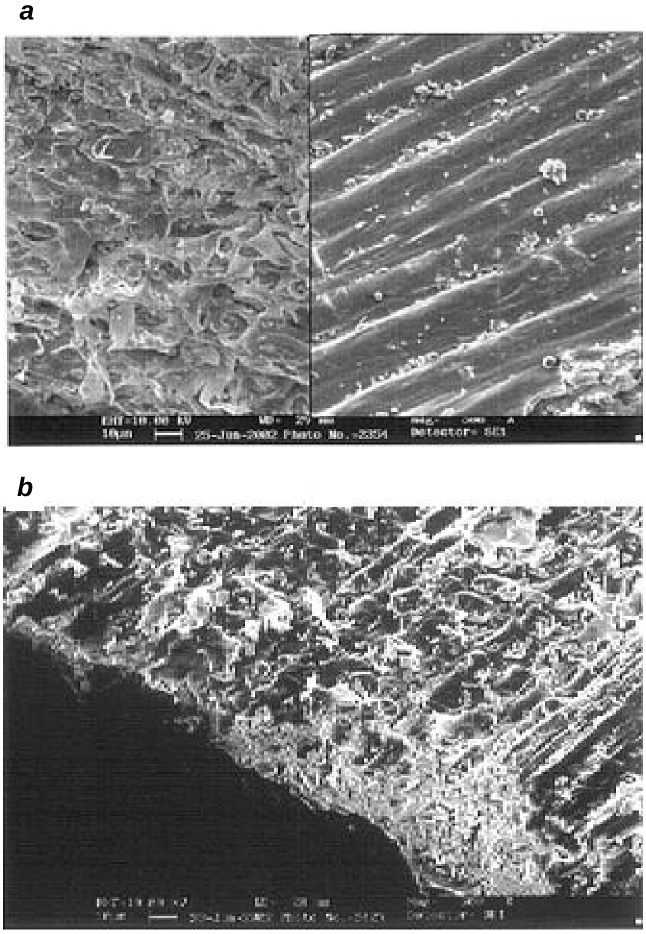

Figure 6. ***a***, SEM image of the surface of a virgin rice husk particle showing longitudinal fibers interspaced within matrix of lignin and cellulose. ***b***, SEM image of the cross-section of a virgin rice husk particle. Dense with no visible porosity.

clearly seen. Also, in all these cases, the aspect ratio increased, though the relative magnitude varied, probably due to the errors inherent in approximating the shapes of the particles to ellipses. These results support the hypothesis that there is a preferential direction for particle shrinkage and this may be due to the structure of the silica skeleton in rice husk particles.

Further heating to 1500°C did not show any change in the particle shape or size. This suggests that the residue is structurally strong and stable. This phenomenon appears to be unique to rice husk and some other straws. However, most other biomass fuels do not exhibit this behaviour[7]. The particle finally softened and melted at temperatures above 1525°C (Figure 5).

To gain additional insight into the particle's structure, we performed scanning electron microscopic (SEM) observations of a rice husk particle undergoing thermal degradation.

To provide samples for SEM experiments, rice husk particles were heated to temperatures between 350 and 850°C in a tube furnace under an inert atmosphere of argon. The temperatures were chosen on the basis of the results obtained from CLSM experiments.

Figure 6 *a* shows the SEM image of a virgin rice husk particle. The structure resembles that of a composite material with fibres regularly interspaced in the matrix. In this case, the fibre is silica and the matrix consists largely of cellulose, hemi cellulose and lignin. Figure 6 *b* shows the cross-section of a virgin rice husk. The transverse section is dense, with no evidence of pores. The longitudinally aligned silica fibres can be seen in Figure 6 *b* and the diameter of theses fibres is between 5 and 10 μm.

The SEM image of a rice husk particle heated to 350°C (Figure 7 *a*) shows the presence of a large number of button-like structures or bumps interspaced with small pores. These were not present initially on the virgin particles. The presence of bumps and pores can probably be explained by the volatiles escaping from the surface as a result of rapid thermal degradation between 250 and 400°C. The bumps could be due to the obstruction of silica fibre to devolatilization. The craters are the regions from where the volatiles have escaped the particle. The transverse-section (Figure 7 *b*) clearly shows the presence of pores. Pyrolysis of the cellulosic material has selectively consumed the matrix leaving the silica fibres behind. Similar exploratory experiments with sawdust particles exhibited complete combustion and little residue remained.

Figure 8 *a* and *b* shows the longitudinal and transverse sections of the particles heated to 850°C. The surface of the particle shows a large number of pores and bumps. This is similar to Figure 7 *a*, except that the number of pores is more and their size larger. In Figure 8 *b*, the pores appear as channels from where the cellulosic material was preferentially removed during pyrolysis and char combustion.

The CSLM experiments combined with SEM observations suggest that the structure of rice husk is similar to a composite material with silica tubes filled with cellulose material constituting the strong-phase and the matrix consisting of lignin. There were no pores in the structure before gasification. However, after exposure to higher temperatures, the silica cylinders remain unaffected by gasification, and there are a large number of pores that are the remnants of pyrolysis and char combustion, These pores appear to have been arranged almost geometrically, suggesting preferential consumption of the matrix material during gasification. Kaupp[7] also reported on the inertness and rigidity of the silica skeleton after thermal degradation. The results on the microstructure of hollow fibres as seen in the transverse section of rice husk after exposure to high temperatures, and the structure of virgin rice husk with elongated silica fibres have not been reported earlier. These images also confirm the earlier observations of other researchers about the inertness of silica.

It appears that the role of silica is more than just a geometric shield to the combustible material in the sample. If

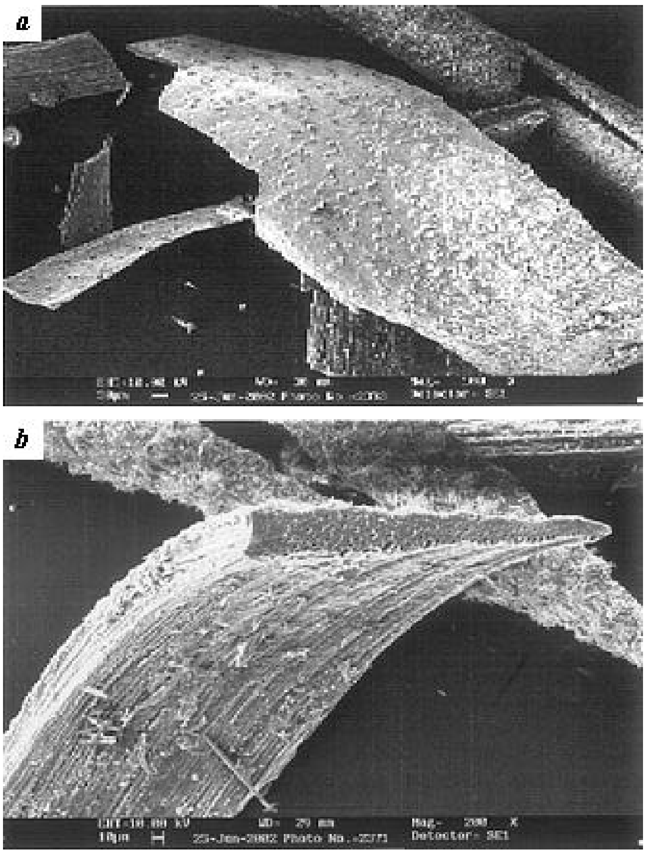

Figure 7. ***a***, Surface of a particle heated to 350°C showing large number of button-like structures or bumps interspaced with small pores. ***b***, Cross-section of particle heated to 350°C clearly showing pores created as a result of pyrolysis.

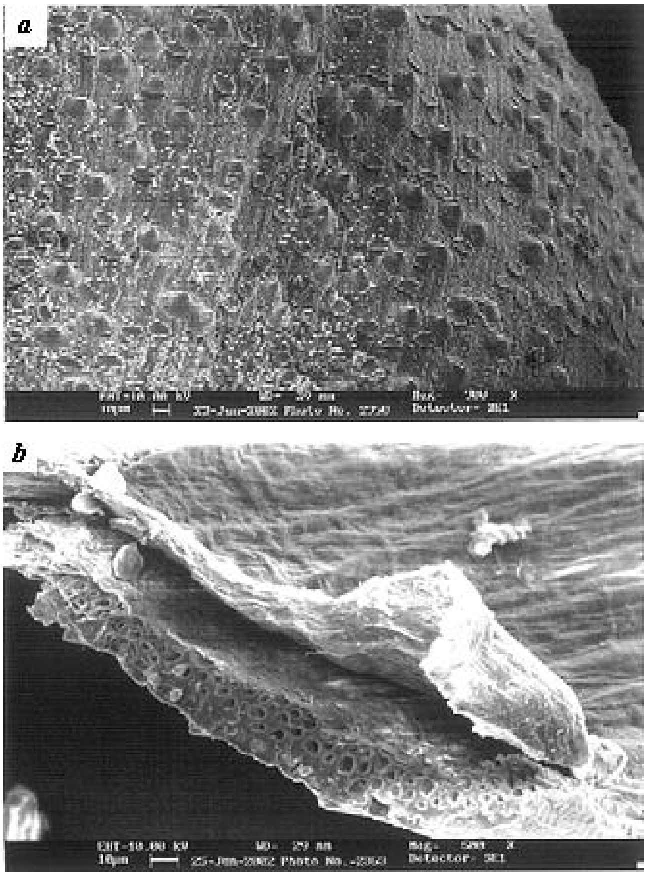

Figure 8. ***a***, Surface of rice husk heated to 850°C showing bumps and pores. ***b***, Cross-section of rice husk particles heated to 850°C.

silica were geometrically shielding the carbon, fluidized bed combustion could have yielded in better carbon conversion since it improves the comminuting of particles in the bed, thus exposing fresh surfaces for gasification. It appears that silica forms molecular bonds with carbon, which are not easily broken at the gasification temperatures. Reactions leading to the formation of silicon carbide from silica involve very high temperatures (above 2500°C) and gasification temperatures are not high enough for such reactions to take place.

In view of these results, we suggest that full carbon conversion in rice husk may not be achievable. However, this does not diminish the importance of rice husk as a fuel source because of its widespread and large availability at affordable prices.

1. Jenkins, B. M., *Physical Properties of Biomass*, Gordon and Breach, New York, 1989.
2. Natarajan, E., Nordin, A. and Rao, A. N., Overview of combustion and gasification of rice husk in fluidized bed reactors. *Biomass Bioenergy*, 1998, **14**, 533.
3. Department of Agriculture and Cooperation, Ministry of Agriculture, Government of India, New Delhi, 2000; http://agricoop.nic.in/.
4. Ministry of Non Conventional Energy Sources, Government of India, New Delhi, 2002; http://mnes.nic.in/.
5. Mukunda, H. S., Pers commun, Indian Institute of Science, Bangalore, 2002.
6. Mukunda, H. S., Shrinivasa, U., Paul, P. J., Dasappa, S. and Rajan, N. K. S., Indian Institute of Science, Bangalore, 2002; http://fmb.no/ arnt/elspa/stand-alone.html
7. Kaupp, A., *Gasification of Rice Hulls: Theory and Practice*, Friedrick Vieweg & Son, 1984.
8. Flanigan, V. J., Xu, B. Y. and Huang, E., Tenth Annual Energy Sources Technology Conference and Exhibition, Dallas, TX, USA, 1987.
9. Bingyan, X. and Zongan, L., Advances in Solar Energy Technology Biennial Congress, Hamburg, Germany, 1987.
10. Xu, B. Y., Huang, W. C., Flanigan, V. J. and Sitton, O. C., Symposium on Energy from Biomass and Waste IX, Chicago, IL, USA, 1985.
11. Sheppard, C. J. R., *Confocal Laser Scanning Microscopy*, New York, 1997.
12. Mansaray, K. G. and Ghaly, A. E., Agglomeration characteristics of alumina sand rice husk ash mixtures at elevated temperatures. *Energy Sources J.*, 1997, **19**, 989.

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