

SILICA FROM RICE HUSK THROUGH THERMAL DECOMPOSITION

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(Received 9 July 1985)

ABSTRACT

The thermal decomposition characteristics of rice husk have been investigated by dynamic thermoanalytical techniques: DTA, TG, DTG and isothermal heating. The observed thermal behaviour is explained on the basis of a superposition of the decomposition of cellulose and lignin, which are the major organic constituents of rice husk. Morphological features of silica in husk as well as the ash are examined by scanning electron microscopy. Silica in the residual ash has been characterised by X-ray diffraction and infrared spectroscopy. Controlled thermal decomposition of rice husk has been shown to be a convenient method for the liberation of silica.

INTRODUCTION

Rice constitutes more than 50% of the diet of about 1.6 billion people, uses about 11% (145 million hectares) of the world's arable land, and was produced to the extent of about 411 million tonnes of paddy in 1982 [1]. One fifth by weight of this paddy consists of husk and constitutes the largest milling by-product of rice.

Rice husk which is, therefore, a major agricultural waste, is a fibrous material with a high silica content. The major constituents of rice husk are cellulose, lignin and ash. Though the actual composition is variable, the following values may be considered typical [2]: ash, 20%; lignin, 22%; cellulose, 38%; pentosans, 18%; and other organics, 2%.

The ash obtained by destruction of organic matter in the husk has a high melting point and high porosity. The ash contains nearly 95% silica and is an important renewable source of silica. Silica in rice husk shows a high reactivity. For instance, rice husk ash with suitable characteristics can combine with lime to yield a cementitious material, which can be a substitute for Portland cement in many applications. Rice husk is also finding use as a source for metallurgical- and semiconductor-grade silicon [3,4].

Controlled combustion could be a convenient method for the release of silica from rice husk but the properties of silica and SiO_2 :C ratio in the residue depend significantly on the conditions prevailing during combustion.

It is therefore desirable to have a detailed picture of the thermal decomposition characteristics of rice husk in both oxidising and non-oxidising atmospheres. However, very little information is available on this aspect except one report [5], which is quite incomplete. This communication is a part of a series devoted to rice husk, its thermal decomposition, and the reactivity of the decomposition products. In particular, it deals with our systematic investigation of the thermal decomposition of rice husk and a preliminary characterisation of the residual silica-rich ash.

EXPERIMENTAL

Materials

The rice husk sample is from the Extension Centre of ASTRA (Centre for the Application of Science and Technology to Rural Areas). The sample of fumed silica is Santocel silica aerogel from M/s Monsanto Co., U.S.A.

Husk is washed well with distilled water to remove adhering soil and clay. It is first dried at ambient temperature and later at about 353 K in an air oven. Dried husk is powdered to 80 mesh size and the powder was employed in the thermal study.

Methods

Thermal analyses were carried out on a combined TG-DTG-DTA unit (ULVAC TA 1500 in conjunction with TGD 5000). About 5 mg of sample was placed in a platinum cup for each analysis.

Infrared spectra in the 200–4000 cm^{-1} region were recorded in alkali halide pellets on a Perkin-Elmer 597 spectrometer.

X-ray diffractograms were recorded with a Philips PW 1050/70 diffractometer with a vertical goniometer, copper K_{α} radiation and a scan rate of $2^{\circ} \text{min}^{-1}$.

Electron micrographs were obtained with a Cambridge Stereoscan 150 scanning electron microscope.

RESULTS AND DISCUSSION

Thermograms of rice husk in static air are shown in Fig. 1 (a', b', c'). It is clear that there are three stages in the decomposition, which are shown on the TG, DTG and DTA curves. Figure 2 shows the TG curves for the thermolysis of husk in a flowing oxygen atmosphere. The effect of oxygen flow rate on DTA is shown in Fig. 3. Oxygen flow rate enhances the magnitude of the first exotherm and the second weight-loss step. Flowing air

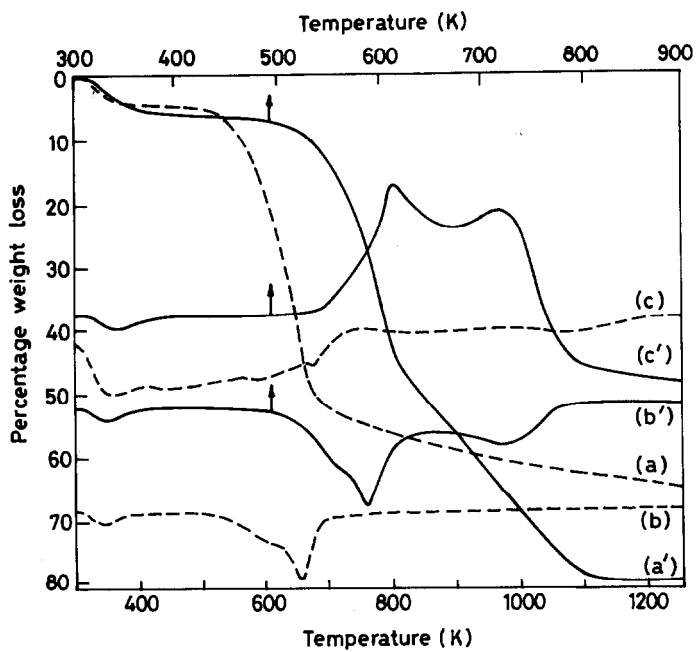


Fig. 1. (a), (b), (c) TG, DTG and DTA of rice husk in flowing nitrogen; (a'), (b'), (c') in static air.

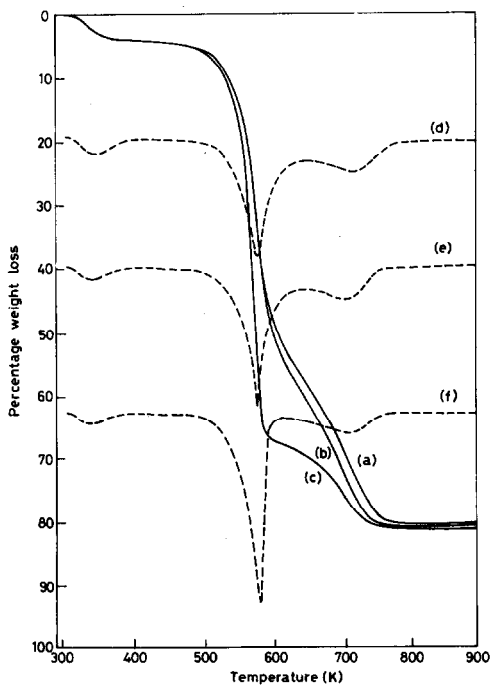


Fig. 2. TG and DTG of rice husk in flowing oxygen at flow rates of: (a), (d) 0.31 h^{-1} ; (b), (e) 0.91 h^{-1} ; (c), (f) 1.81 h^{-1} .

has a similar effect on the thermograms. The thermograms are quite different in a non-oxidising atmosphere like nitrogen (Fig. 1a, b, c). The DTA shows a small endotherm in place of the prominent exotherm (first peak) observed in oxidising atmospheres, and this endotherm is followed by an exothermic shift. The decomposition is incomplete even at 1273 K. The weight of the residue at this stage is $\sim 35\%$ compared to 20% for complete decomposition of the organic constituents.

Irrespective of the surrounding atmosphere, there is an initial weight loss of $\sim 6\%$ below 373 K, followed by a rapid weight loss of $\sim 45\%$, starting at ~ 533 K. This loss reaches $\sim 65\%$ in an oxygen atmosphere. The residue in nitrogen atmosphere is black, while all other residues are white ashes.

The observed features of the thermal decomposition of rice husk can be explained on the basis of the decomposition behaviour of its major constituents: cellulose, lignin and ash (mostly silica). Thermal decomposition behaviour of cellulose and lignin have been investigated in relation to the pyrolysis of wood. Cellulose and lignin are reported to decompose in the temperature ranges 600–650 and 500–773 K, respectively [6]. Further, it is reported that DTA of cellulose in air shows two [7–9] or three [10] exothermic peaks. The first peak is attributed to combustion of volatile material released in the degradation process, the second caused by glowing combustion of carbonaceous residue, and the final exotherm is probably due to the combustion of product gases. In the TG of cellulose, major weight loss

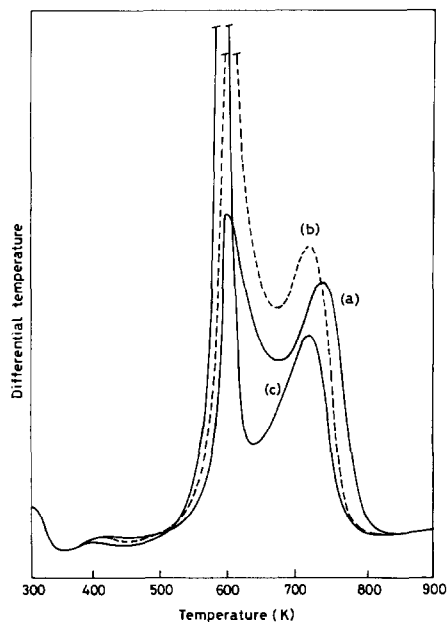


Fig. 3. DTA of rice husk in oxygen at flow rates: (a) 0.3 l h^{-1} , (b) 0.9 l h^{-1} and (c) 1.8 l h^{-1} .

is attributed to the production of combustible volatiles, which is identical both in air and nitrogen atmospheres. Lignin is reported [11] to decompose in the range 635–755 K with a DTG peak at ~ 735 K. In the decomposition of wood, lignin is supposed to contribute mainly to the char fraction, which burns slowly and is probably responsible for increased carbon loss between 625 and 675 K.

In the decomposition of rice husk, the weight loss in the temperature range 325–375 K is attributed to the loss of sorbed water. The second and major mass loss of nearly 45–65% is attributed to the breakdown of the cellulose constituent to combustible volatiles, water, carbon dioxide and char. The volatiles in the presence of oxygen undergo flaming combustion giving rise to the first exotherm in DTA (Fig. 1).

Char gives rise to glowing combustion. It can be noted on Fig. 1, that the DTG peak occurs at a slightly lower temperature than the first exothermic peak in DTA. This clearly indicates that volatilization precedes combustion. The relative proportion of the two combustion modes depends on the availability of the oxidant. This is brought about quite clearly in Fig. 3, where the magnitude of the first exothermic peak is seen to be strongly dependent on the oxygen flow rate. Oxygen helps the formation of volatile oxygenated species and the volatile organics burn more rapidly, generate more heat and promote rapid and more complete combustion of the lignocellulosic material by increasing the local temperature and the rate of gasification. There is an overlap of the second stage of cellulose decomposition and the decomposition of lignin. The DTG peak at ~ 735 K corresponds to the decomposition of lignin. This agrees with the reported [10] decomposition behaviour of lignin. In the decomposition of cellulose there is also a peak around this temperature. Hence, the second exothermic peak at ~ 735 K is considered to be a composite peak representing the combustion of both cellulose and lignin. The observed thermal effects are, however, dominated by the thermal effects accompanying the decomposition of the cellulose fraction.

Isothermal heating of rice husk at 475 K for 5 h produces a weight loss of only 6.89%. There is no other change and this weight loss corresponds mainly to the loss of sorbed water. Heating husk at 510 K for 5 h results in a weight loss of 15.48% and a visible blackening. Evidently, at this temperature the decomposition of the organics, probably cellulose, has taken place to a certain extent. The residues obtained by isothermal heating of husk at 575 and 675 K are black and white, respectively. The infrared spectra of rice husk and the residues obtained from isothermal heating of husk are shown in Fig. 4. The appearance of an absorption band at ~ 1720 cm^{-1} and decrease in intensity of the bands at ~ 1510 and ~ 2950 cm^{-1} indicate the progress of decomposition of organics from the husk. Their disappearance is an indication of the completion of decomposition of the organic constituents. Comparison of the IR spectrum of cellulose with those of husk and partially

decomposed husk emphasises the dominant role of the decomposition of the cellulose fraction. The peak at $\sim 1720\text{ cm}^{-1}$ is attributed to the growth and development of the C=O band and the band at $\sim 1620\text{ cm}^{-1}$, could be assigned to either C=C vibration or to O-H stretching of adsorbed water. These features compare well with the IR spectra of partially combusted char obtained during the combustion of cellulose [12]. The residue obtained at 675 K has a spectrum similar to that of fumed silica. It can be concluded that on isothermal heating a minimum of 675 K is required for the complete destruction of the organic matter from rice husk and to liberate silica. All the residues and the powdered husk give rise to a broad hump around $22.2^\circ 2\theta$ in their X-ray diffractograms, indicating the amorphous nature of the silica present in them.

There is considerable disagreement regarding the nature and structure of silica in rice husk and residual ash. Silicon occurs in the husk as a hydrated amorphous form of silica and this is variously described as opaline, glassy or gel-like [13]. The X-ray evidence favours the presence of silica in the form of disordered cristobalite.

Figure 5 presents electron micrographs of rice husk and of ash obtained by heating the husk in air at 775 K for 12 h. Figures 5a and b show the outer and inner surfaces of the husk. Corrugated outer epidermis and thin lamellar inner epidermis are clearly visible. In Fig. 5c the outer epidermis is imprinted

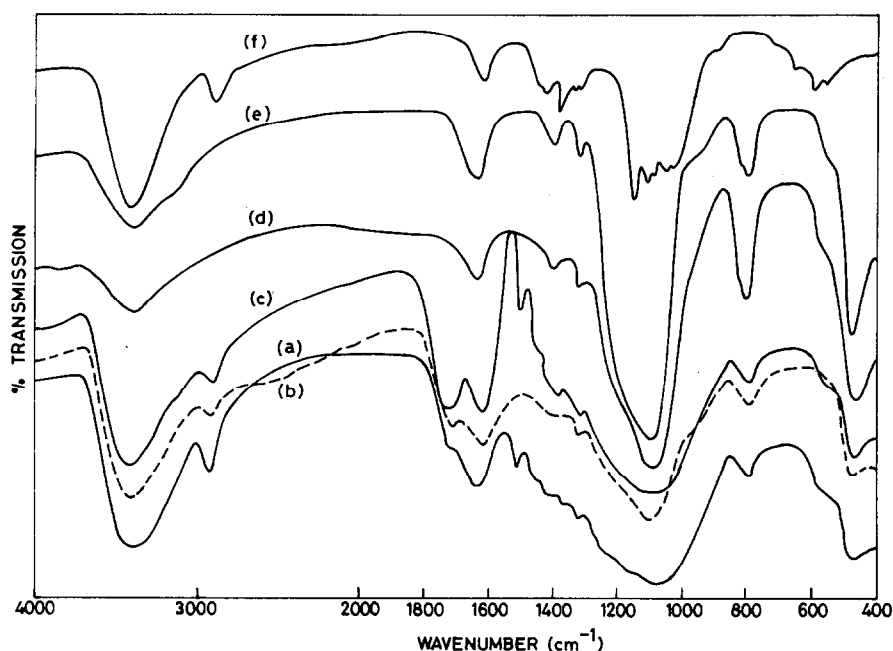


Fig. 4. Infrared spectra of (a) rice husk, (b) ash at 510 K, (c) ash at 575 K, (d) ash at 675 K, (e) fumed silica and (f) cellulose.

on the silica skeleton, while in Fig. 5d the thinner inner epidermis has been broken up during the thermal decomposition of the organic binders thus leaving a highly porous structure. Figure 5f shows the lamellar structure of

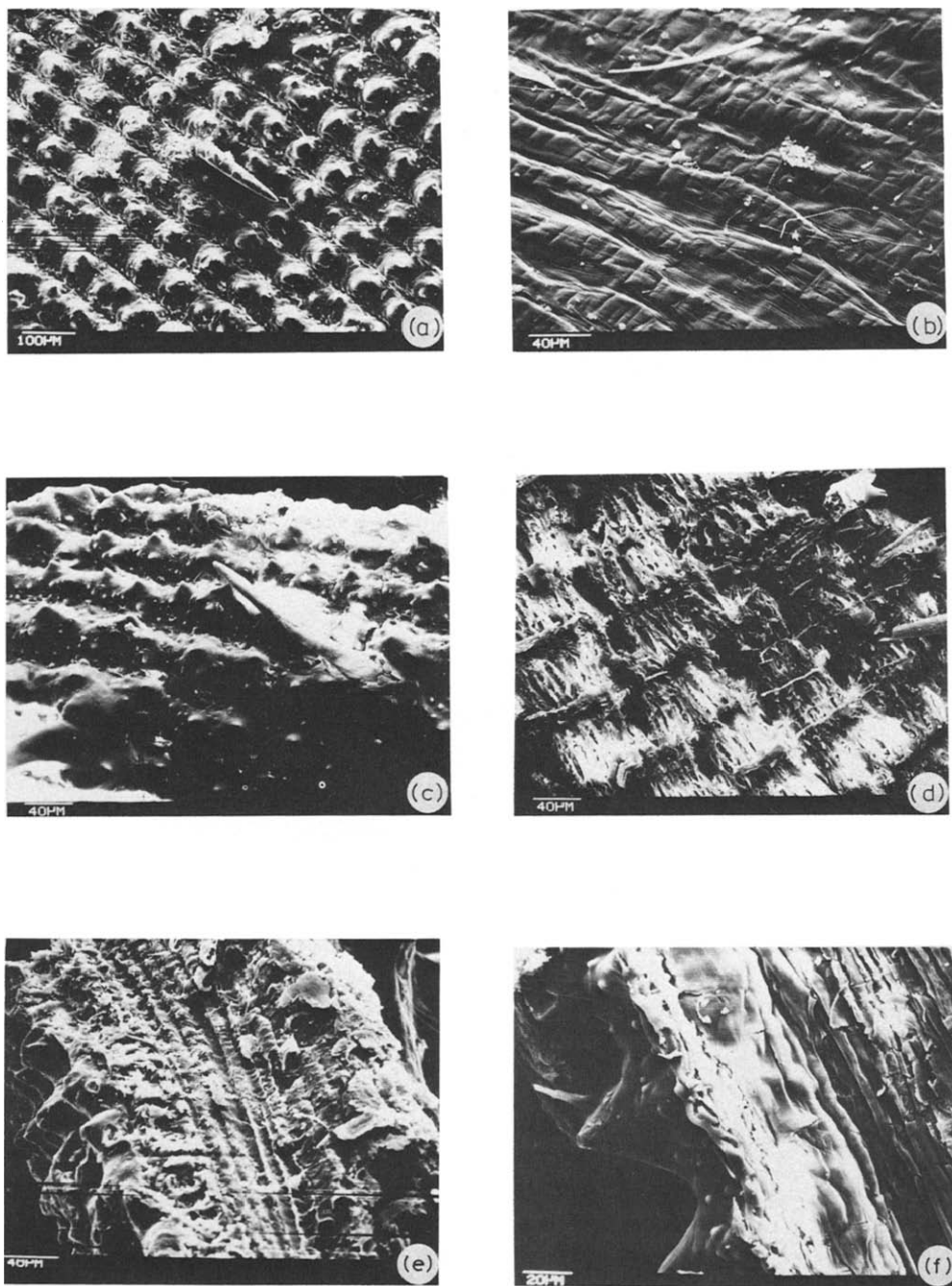


Fig. 5. Electron micrographs of (a), (b) outer and inner surface of husk; (c), (d) outer and inner surface of ash; (e), (f) cross-section of husk and ash.

the silica deposit. The lamellae are of varying thickness. The same structural features can be seen in Fig. 5e which is a cross-section of the husk. Further, the micrographs indicate that the distribution of silica in the husk is not haphazard, but follows a set pattern. Similar microstructural features have been reported [14] for silica samples released from rice husk by acid treatment. Hence, it can be inferred that controlled thermal decomposition of rice husk at relatively low temperatures leaves the silica skeleton undamaged.

Mapping of the silica deposit in the husk requires EDAX (energy dispersive analysis of X-rays). While we were contemplating this, a recent publication [15] has reported precisely this feature of rice husk. It is reported that silica is primarily concentrated within the outer epidermis towards the middle of the husk structure, a small but significant amount of silica was found to reside within the inner epidermis adjacent to the rice kernel. By inference we can conclude that the mounds in Fig. 5c and the lamellar patches in Fig. 5d as well as the lamellae in Fig. 5e and f, consist of silica deposits. This is also corroborated by the composition of the ash, which consists of nearly 95% silica.

ACKNOWLEDGEMENTS

We wish to thank our colleague Professor A.K.N. Reddy for his keen interest and encouragement during this investigation and Materials Research Laboratory for extending XRD and electron microscopy facilities.

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