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# Production of amorphous silica and combustible gas from rice straw

A. CHAKRAVERTY, S. KALEEMULLAH
*Post Harvest Technology Centre, Indian Institute of Technology, Kharagpur 721 302, India*

Results of the thermogravimetric analysis of untreated and 1 N HCl-treated rice straw reveal that mass loss occurred in three distinct stages: removal of moisture; release of volatile matter and oxidation of fixed carbon. The rate of combustion of fixed carbon of acid-treated straw was faster than that of untreated straw. Studies on the combustion of large samples of straw in a vertical electric furnace showed that both amorphous silica and combustible gas could be produced simultaneously under certain conditions. Acid treatment of straw prior to combustion helped in producing a white ash in a short period. The silica produced at a furnace temperature of 500 °C with a maximum bed temperature of 720 °C was amorphous in nature. The low-calorie combustible gas could be produced when straw containing 6.5–7.5% moisture was fed to the furnace set at a temperature above 450 °C. The flame temperature, as well as the duration of the flame, increased as the bed thickness increased. A furnace temperature of 450 °C, a bed depth of 20 cm and a combustion period of 3 h are considered as optimum for the production of white amorphous silica from 1 N HCl-acid-treated straw.

## 1. Introduction

Rice-straw ash contains 69.1–76.8% silica [1]. The carbon-free pure amorphous silica (white ash) obtained from rice husks can be utilized for the production of silicon. It has also been reported that the acid leaching of rice husks helps in the removal of the most of the metallic impurities for the production of pure amorphous silica [2]. However, very little information is available on the production of amorphous white ash along with low-calorie combustible gas from rice straw. Therefore a project was undertaken with the following objectives: to study the thermal degradation of straw and acid (1 N HCl)-treated rice straw at a heating rate of 5 °C $min^{-1}$; to study the effects of acid leaching of rice straw, furnace temperature and straw-bed thickness on the production of low-calorie gas and amorphous white silica and to study the structural nature of the above rice-straw silica using X-ray diffractometry.

## 2. Experimental procedure

The chopped rice straw was thoroughly wet-cleaned and dried. After leaching of the sample with 1 N HCl at 75 °C for 1h, it was thoroughly washed with distilled water and then dried in the sun so that its moisture was reduced to about 6.5%(wb). The raw and acid-treated ground samples (40 mesh) were used for thermogravimetric analysis (TGA) in still air, whereas the same unground samples were used in a vertical furnace for the simultaneous production of amorphous white ash and low-calorie gas.

For TGA, 260–310-mg samples were heated at a rate of 5 °C $min^{-1}$ from ambient temperature to 750 °C. The TGA technique was applied to determine the threshold decomposition temperature and the rate of degradation of different constituents in the straw sample.

A vertical fixed-bed electric furnace equipped with thermocouples in conjunction with a temperature controller *cum* indicator, a temperature recorder and a digital multimeter was used. The following method of burning straw in the vertical electric furnace was used to produce white ash and low-calorie combustible gas simultaneously. The furnace temperature was raised and set at the desired stable temperature. Then straw was charged into the furnace and subjected to the set temperature with natural air flow. Combustion continued until the whole mass turned into white ash.

The residual carbon content present in ash was determined by taking a known quantity of ash in a silica crucible and keeping it inside the muffle furnace set at 700 °C for 24 h. The mass loss was taken as the residual carbon content of the ash.

The structure of silica in white ash was examined by X-ray diffraction (XRD) at a chart speed of 2° $min^{-1}$ using $CuK_{\alpha}$ radiation to determine the formation of any crystalline silica during the combustion of straw at high temperatures.

## 3. Results and discussion

### 3.1. Thermogravimetric analyses

The TGA curves of untreated and acid-treated samples are shown in Figs 1 and 2. The TGA curves indicate that the mass loss occurred in three major stages during thermal decomposition: (i) removal of



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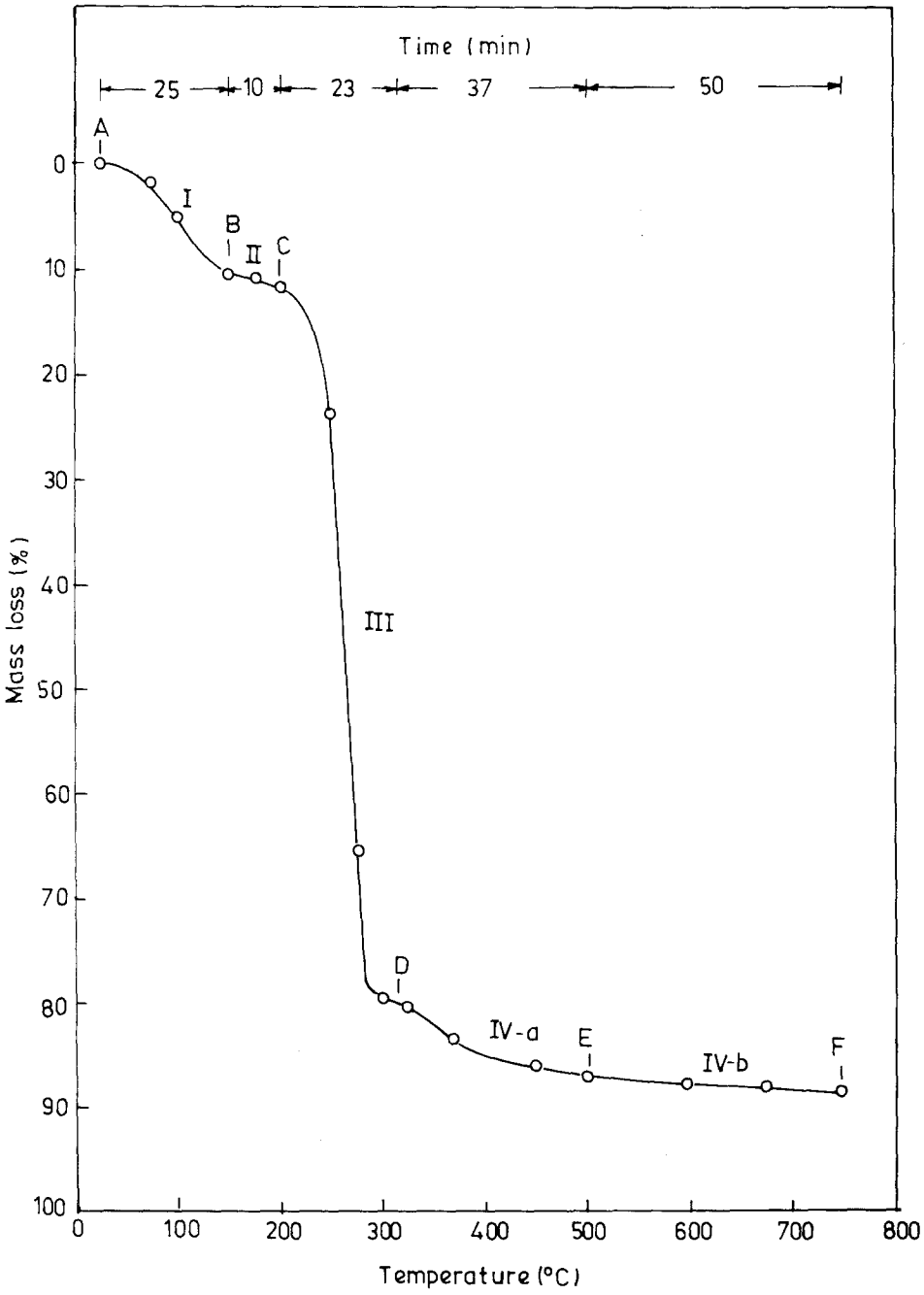


*Figure 1* TGA curve of ground and untreated straw. Sample mass, 301.7 mg; heating rate, 5 °C $min^{-1}$.

moisture; (ii) removal of volatile matter and (iii) oxidation of fixed carbon. Beside these three stages, there were two sub-stages: all stages are marked in the Figs 1 and 2 as A–B, B–C, C–D, D–E and E–F. The temperature ranges of different stages are given in Table I. The percentage and rate of mass loss in each stage, as calculated from the TGA curves, are indicated in Table II.

The TGA curves show that the temperature ranges of the same stages were sometimes different for untreated and acid-treated straw. The mass loss of 10–10.5% in the first stage took place in the temperature range 25–150 °C, and corresponds to the removal of moisture from the material. The second stage occurred in the range 150–200 °C with a hardly appreciable mass loss of 0.5–1%. This was considered as the transition stage. The major part of the mass loss took place in the third stage, in the range 175–325 °C, indicating a steep fall in the TGA curve. The mass loss of 60–68% in this stage was due to the removal of volatile matter. The mass losses and the temperature ranges of substages IVa and IVb were 7.5–17.75 and 1.5–2.25%, and 315–500 and 500–750 °C, respectively. The mass loss in this stage was due to slow combustion of solid (fixed) carbon. From Table I it is also clear that the minimum temperature required for the oxidation of fixed carbon ranges from 315 to 325 °C. This implies that the minimum furnace temperature should be above 325 °C for complete combustion of rice straw to obtain silica.

The mass loss in stage III was 68% for untreated straw and 60% for acid-treated straw. Therefore the mass loss in stage III was less in the case of treated than untreated straw. This clearly indicates that some percentage of volatile matter had been leached away when the straw was leached with 1 N HCl at 75 °C and washed away with distilled water. The rate of release of volatile matter was 2% $min^{-1}$ for treated straw, and 2.96% $min^{-1}$ for untreated straw due to the presence of more volatile matter.

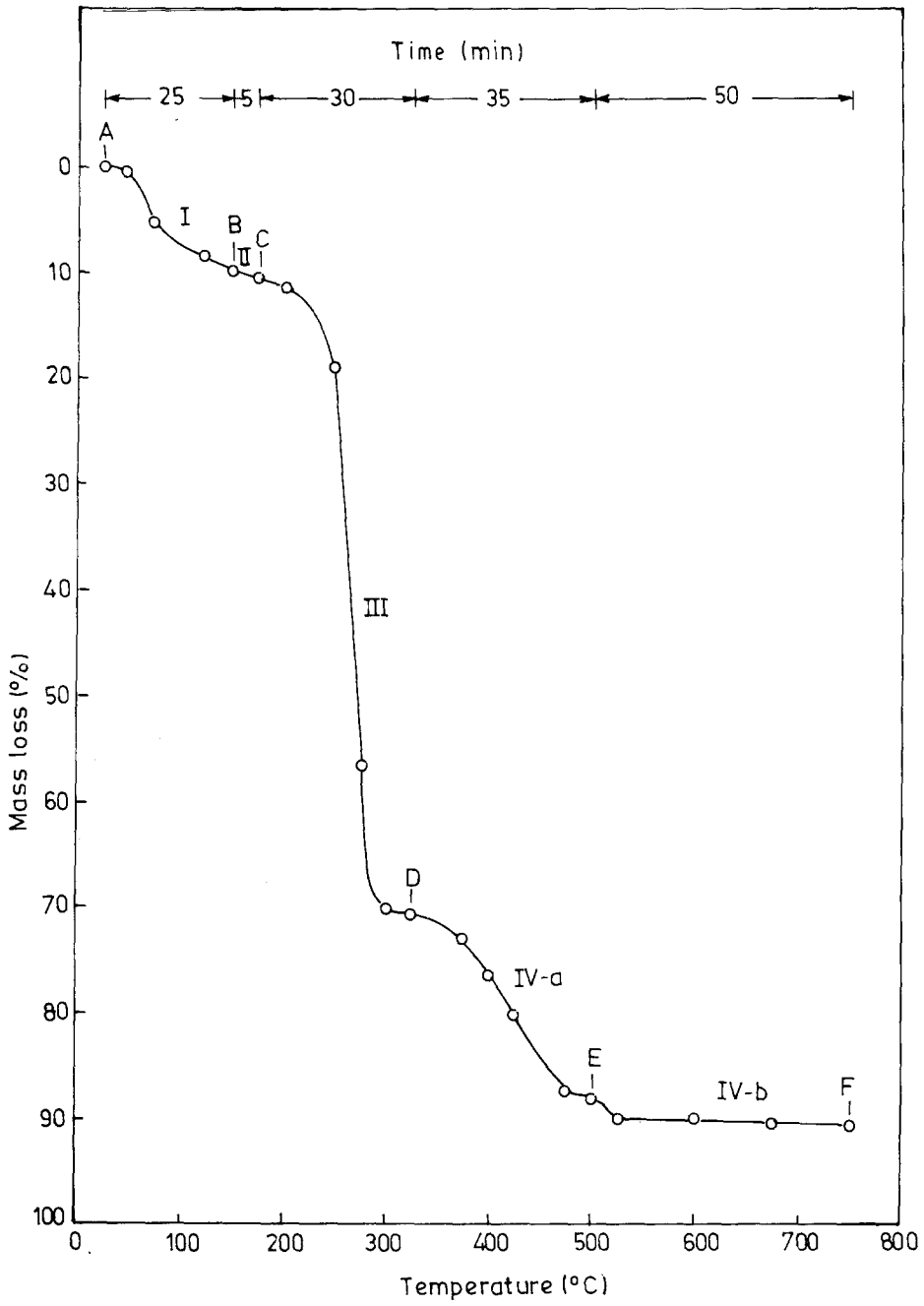


*Figure 2* TGA curve of ground and treated straw. Sample mass, 269.1 mg; heating rate, 5 °C min$^{-1}$.

TABLE I Temperature range for different stages of mass loss in the TGA curves

| Treatment | Heating rate (°C min$^{-1}$) | Temperature range in different stages (°C) | | | | |
|---|---|---|---|---|---|---|
| | | I | II | III | IVa | IVb |
| Untreated | 5 | 25–150 | 150–200 | 200–315 | 315–500 | 500–750 |
| 1 N HCl-treated | 5 | 25–150 | 150–175 | 175–325 | 325–500 | 500–750 |

TABLE II Percentage and rate (% min$^{-1}$) of mass loss at different stages in the TGA curves

| Treatment | Heating rate (°C min$^{-1}$) | I | | II | | III | | IVa | | IVb | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | % | Rate | % | Rate | % | Rate | % | Rate | % | Rate |
| Untreated | 5 | 10.5 | 0.42 | 1.0 | 0.1 | 68.0 | 2.96 | 7.5 | 0.203 | 1.5 | 0.03 |
| 1 N HCl-treated | 5 | 10.0 | 0.4 | 0.5 | 0.1 | 60.0 | 2.0 | 17.75 | 0.507 | 2.25 | 0.045 |

The mass loss in stage IV was higher for treated (20%) than untreated (9%) straw. The rates of mass loss of fixed carbon were 0.235% $min^{-1}$ and 0.104% $min^{-1}$, respectively, for acid-treated and untreated straw. This clearly indicates that the rate of combustion of fixed carbon was faster for the acid-treated than untreated straw.

## 3.2. Production of low-calorie gas

From Table III, it is clear that the gas which came out after heating straw at a set temperature of 450 °C gave flame temperatures of 650, 670 and 720 °C for about 5, 9 and 13 min at 20-, 30- and 40- cm bed depths, respectively. At 500 °C set temperature, the gas gave flame temperatures of 660, 710 and 760 °C for about 7, 10 and 15 min for bed thicknesses of 20, 30 and 40 cm, respectively.

Therefore at a particular furnace temperature the duration and temperature of the flame increase as bed thickness increases. Also, at a certain bed depth the flame temperature increases with the increase in furnace temperature.

## 3.3. Production of amorphous white ash with natural draught

The data on straw-bed temperature against time at each of the furnace temperatures of 450 and 500 °C at 40 cm bed depth are plotted in Figs 3 and 4. The consolidated data on combustion time, energy spent, residual carbon, maximum bed temperature and production cost are shown in Figs 5–7. Figs 3 and 4 show that the furnace temperatures increased from ambient to 450 and 500 °C in 45 min and 1h, respectively. When straw was fed to the furnace, initially the straw bed temperature increased sharply and reached the maximum value, and then started falling to a level close to the furnace set temperature. These figures also indicate that the general pattern of the straw bed temperature was almost the same for all furnace temperatures and bed thicknesses, except that the duration of maximum bed temperature increased as the bed thickness increased.

From Figs 5–7, it is clear that for 20-, 30- and 40- cm bed depths at 450 °C furnace set temperature, the corresponding maximum straw-bed temperatures recorded were 690, 700 and 710 °C. It took 7, 14 and

TABLE III Effect of furnace set temperature and straw-bed depth on the production of low-calorie gas

| Mode of burning | Furnace set temperature (°C) | Bed depth (cm) | M. C. of straw (% wb) | Gas flame temperature (°C) | time (min) |
|---|---|---|---|---|---|
| Furnace temperature raised from ambient and set at the desired high temperature | 450 | 20 | 6.5 | 650 | 5 |
| | | 30 | 6.8 | 670 | 9 |
| | | 40 | 7.0 | 720 | 13 |
| | 500 | 20 | 7.1 | 660 | 7 |
| | | 30 | 6.9 | 710 | 10 |
| | | 40 | 6.7 | 760 | 15 |

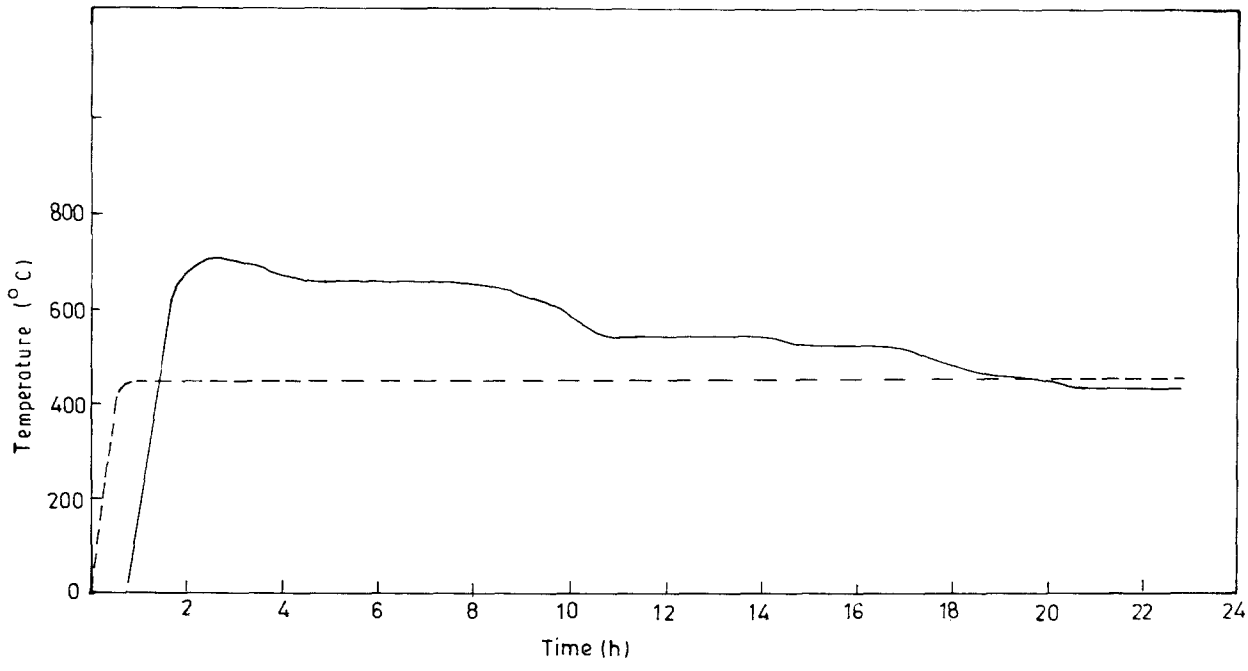


*Figure 3* Effect of furnace temperature set at 450 °C (- - -) on untreated straw-bed temperature (——) for 40 cm bed depth.

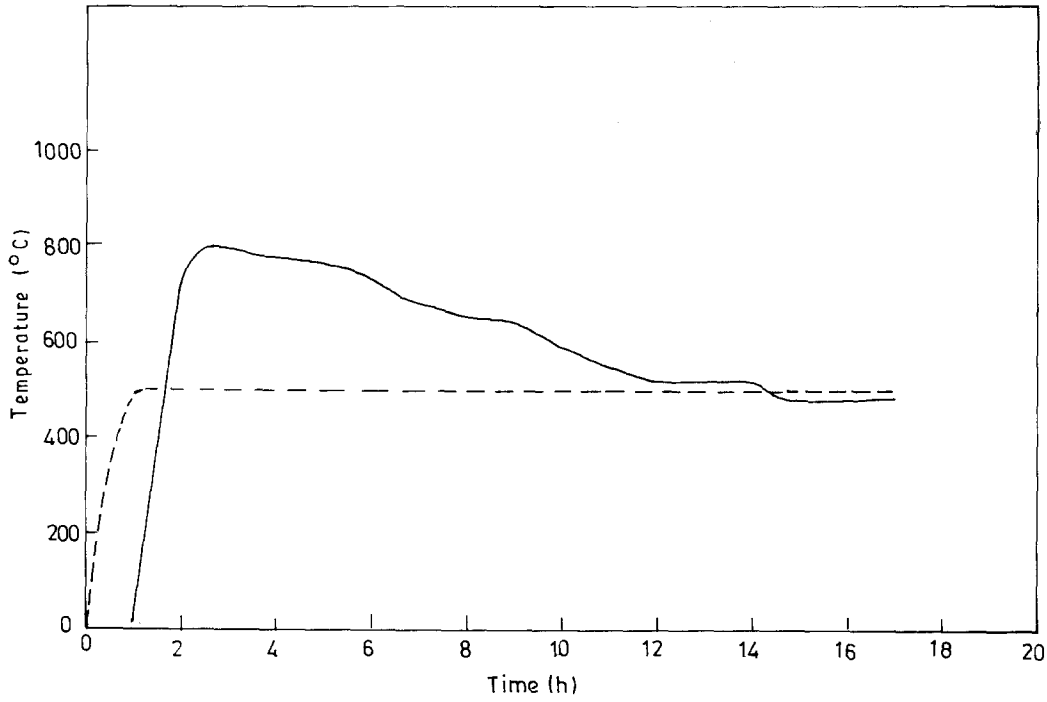


*Figure 4* Effect of furnace temperature set at 500 °C (- - -) on untreated straw-bed temperature (——) for 40 cm bed depth.

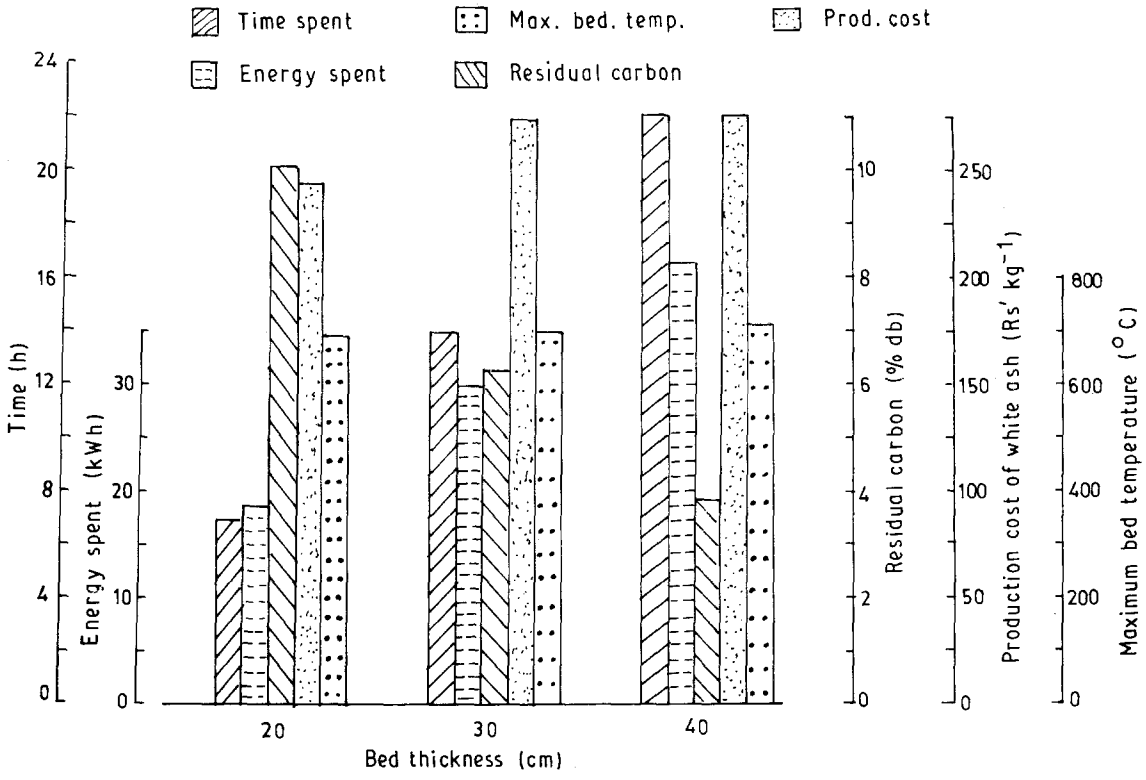


*Figure 5* Effect of bed thickness on time, energy spent, residual carbon in white ash, production cost and the maximum bed temperature for production of amorphous white ash from untreated straw at 450 °C furnace temperature.

22 h, respectively, at the above temperatures for complete combustion of straw, and the residual carbon contents in the corresponding ash samples were 10.06, 6.25 and 3.79% (db). It was observed that in the case of untreated straw, only the top and bottom layers became white but not the middle layers. Although the residual carbon content of one ash sample from untreated straw was 3.79%, its colour remained blackish. It may be noted that the straw contains a higher percentage of metallic impurities [2] which retards combustion and hinders the straw from turning into completely white ash.

At a furnace set temperature of 500 °C, the straw did not become completely white even after exposure for 16 h. It appears that it is necessary to pretreat the raw straw with HCl acid prior to combustion for removal

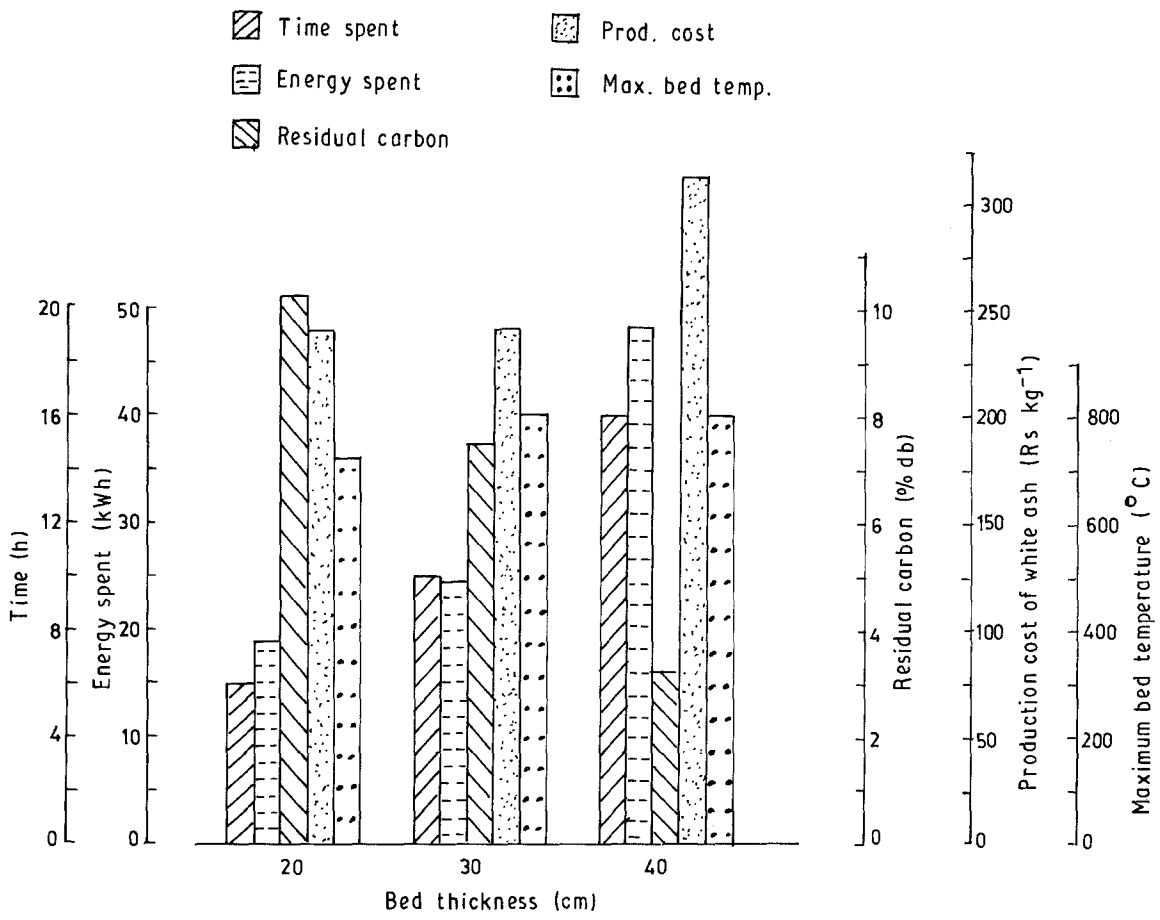


*Figure 6* Effect of bed thickness on time, energy spent, residual carbon in white ash, production cost and the maximum bed temperature for production of amorphous white ash from untreated straw at 500 °C furnace temperature.

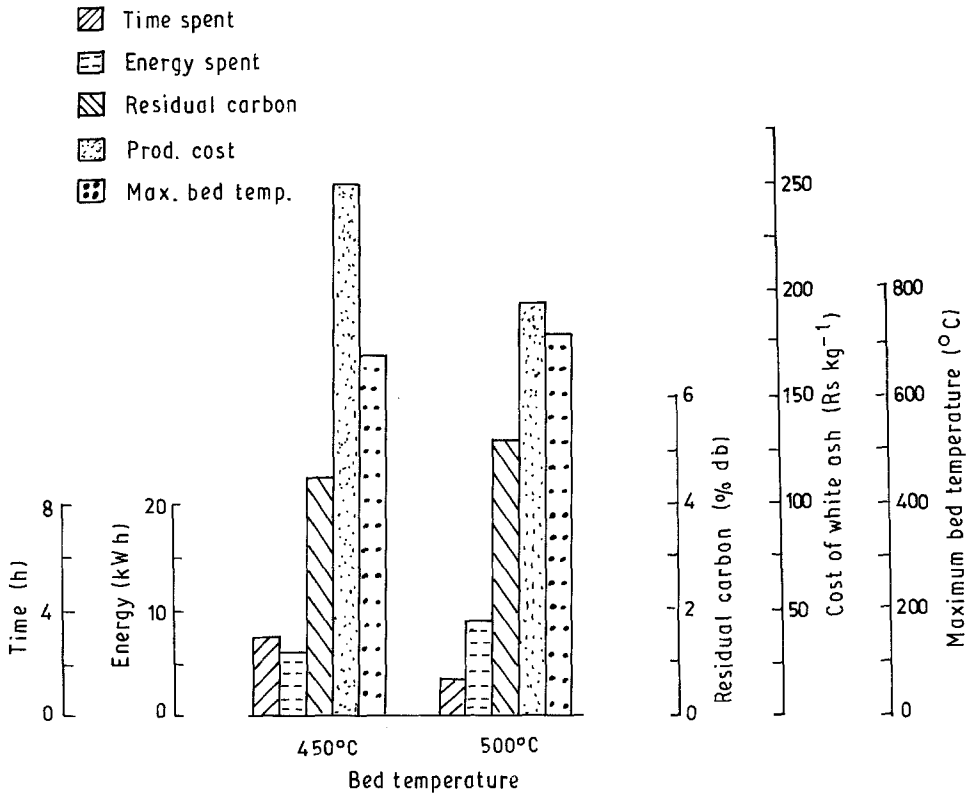


*Figure 7* Effect of furnace temperature on time, energy spent, residual carbon in white ash, production cost and the maximum bed temperature for production of amorphous white ash from treated straw.

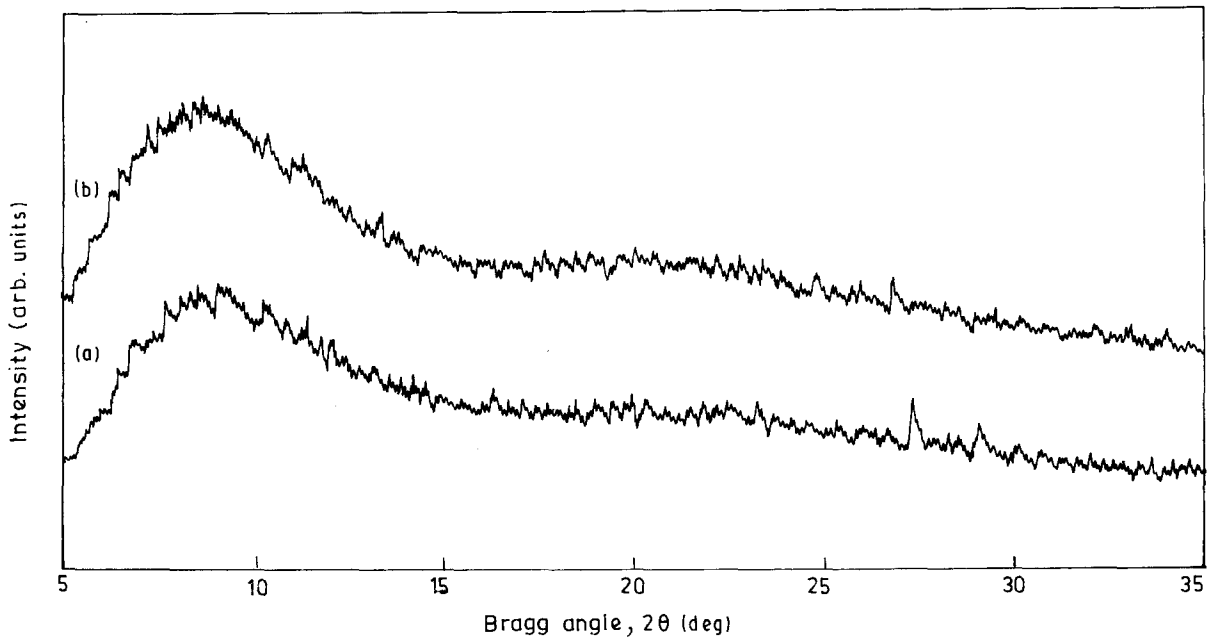


*Figure 8* X-ray diffractograms of white ash obtained after heating rice straw in a vertical furnace at 500 °C. Radiation, Cu$k_\alpha$. (a) Untreated; (b) 1 N HCl-treated rice-straw ash.

of its metallic impurities, to produce pure white silica (ash) within a reasonable period of combustion [3]. The maximum bed temperatures recorded were 720, 800 and 800 °C for 20-, 30- and 40- cm bed depths, respectively at 500 °C furnace set temperature. As the bed temperature went up to 800 °C, the 500 °C furnace set temperature can not be recommended for the production of amorphous silica by combustion of untreated straw, as crystalline silica may be formed at this high temperature [4, 5].

### 3.4. Effect of pretreatment of straw with acid (1 N HCl)

The acid-treated straw samples of 20-cm bed thickness were subjected to combustion at 450 and 500 °C furnace set temperatures. The corresponding combustion times were 3 and 1.5 h, and the maximum bed temperatures were 680 and 720 °C. The ashes obtained were white in colour. It is clear from Figs 5–7 that the combustion times required for 20-cm bed depth at 450 and 500 °C were less for acid-treated than untreated straw.

### 3.5. X-ray diffraction analysis of white ash

The X-ray diffractograms of the two ash samples obtained from untreated and acid-treated straw at 500 °C for 20 cm bed thickness (Fig. 8) do not have a sharp peak; showing that the silica in the above white ash samples was amorphous in nature. The silica in the above ash remained amorphous even at a straw bed temperature of 720 °C.

### 3.6. Optimum combustion conditions

From the standpoint of straw-bed temperature (< 700 °C), reasonable residual carbon content and production cost, a combination of a furnace temperature of 450 °C, bed-depth of 20 cm and combustion period of 3 h appears to be optimum for the production of amorphous silica (white ash) from 1 N HCl acid-treated rice straw.

## 4. Conclusions

1. The thermal degradation of untreated and acid-treated rice straw takes place in three distinct stages of mass loss: removal of moisture, release of volatile matter and oxidation of fixed carbon.
2. The rate of combustion of fixed carbon was faster for acid-treated than untreated rice straw.
3. Acid treatment of rice straw prior to combustion helped in producing white ash in a shorter period.
4. Combustible low-calorie gas was obtained only when the furnace temperature was set above 450 °C and straw of a moisture content between 6.5 and 7.5% was fed to the furnace after attaining the set temperature.
5. The furnace temperature of 450 °C, a bed-depth of 20 cm and a combustion period of 3 h are considered as optimum for the production of milky-white amorphous silica from 1 N HCl acid-treated straw.

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