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STUDIES ON THERMAL DECOMPOSITION OF RICE STRAW

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ABSTRACT

Investigations of the thermal decomposition of untreated rice straw and that treated with HCl and HNO_3 of various concentrations were carried out by thermogravimetry, derivative thermogravimetry and differential thermal analysis. The mass loss occurred in three distinct stages; removal of moisture, release of volatile matter and burning of combustible carbon. The corresponding temperature ranges were 0–200, 275–400 and 400–600 °C. The overall thermal degradation of rice straw was found to be an exothermic process.

INTRODUCTION

Rice straw is a major residue of the paddy crop. Efforts over the years to utilize this material have resulted in minor usage, mostly in low value applications in the agricultural area. Although technologies for a large number of uses of rice straw have been identified in the last few decades, still the most common use of the straw is as animal feed, which is objectionable owing to its bad effect on animals. Untreated rice straw is used as ruminant feed [1]. Rice straw is commonly disposed of by burning in an open field. Disposal can be a particular problem in areas of a country like U.S.A., where the field burning of these materials is no longer permitted because of environmental pollution. The potential health hazards from smoke from rice straw burning showed that the alkaline fraction was the most mutagenic and may be toxic to mammalian pulmonary alveolar macrophages [2]. The industrial utilization of straw has been modest because of uncertainty about the raw material (its variable quality, availability and market price) and the number of farmers and suppliers required.

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In the wake of the global energy crisis, extensive efforts are being devoted to the development of a high volume, low cost and quickly commercializable technology for manufacturing solar grade silicon materials. The rice straw, which is a major agricultural residue and treated as waste, is available in plenty. Rice straw contains silica, some minerals and organic compounds. The silica content of the rice straw is 11–16% [3]. The silica obtained from rice straw ash is amorphous in form. It can be made pure because most of the metallic impurities which rice straw contains can be successfully removed by subsequent acid leaching. This pure silica material offers promise as a low cost source of silicon suitable for making solar cells and semiconductors. Besides this, many other valuable products can also be synthesized from it [4,5].

Therefore, rice straw offers an alternative low cost raw material naturally available in abundance and suitable as a source material for solar-grade polycrystalline silicon. In order to take full advantage of this cheap raw material as a source of various valuable products, it is necessary that a comprehensive study of the thermal decomposition of rice straw for its conversion into amorphous ash-silica should be undertaken.

Keeping the above points in mind, the present research project has been undertaken with the following objectives: (i) to study the thermogravimetric analysis (TGA), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) of untreated and acid-treated rice straw; (ii) to study the structural nature of rice straw ash using X-ray diffractometry and scanning electron microscopy (SEM).

EXPERIMENTAL DETAILS

The rice straw was obtained from a high-yielding variety of paddy. This straw was chopped to a size 1 cm long. The chopped straw samples were thoroughly cleaned with water and then dried. The dried and chopped samples were leached in different concentrations of HCl (1 and 6 N). The temperature used for this treatment was $90 \pm 2°C$ and the time taken was 45 min. After treatment, the straw was thoroughly washed with distilled water and dried. Some chopped straw samples were also treated with different concentrations (1 and 8 N) of HNO_3 at a temperature of $80 \pm 2°C$ for 30 min. After leaching, the straw was thoroughly washed with distilled water and then dried.

The TGA of untreated and acid-treated samples was carried out in still air using a thermogravimetric analyser (made by the Fertilizer Corporation of India). The sample was placed in a platinum crucible and heated at a constant rate of $2°C\ min^{-1}$ from an ambient temperature until a constant mass was obtained.

The thermogravimetry (TG), DTG and DTA of the untreated and acid-treated straw were performed using a thermal analyser (Mettler TA 2000 system) under static ambient conditions. Platinum crucibles were used as sample holders and heat-treated α-Al_2O_3 was used as the reference sample. The furnace temperature was programmed at 20 °C min^{-1} from an ambient temperature of 25 °C until a constant weight was attained. The TG, DTG and DTA curves were recorded simultaneously together with the temperature rise.

RESULTS AND DISCUSSION

TGA at a heating rate of 2 °C min^{-1}

Results of TGA studies of various rice straw samples are reported. The overall TGA of untreated and acid-treated rice straw revealed that the decrease in mass loss with the rise in temperature takes place in a number of stages.

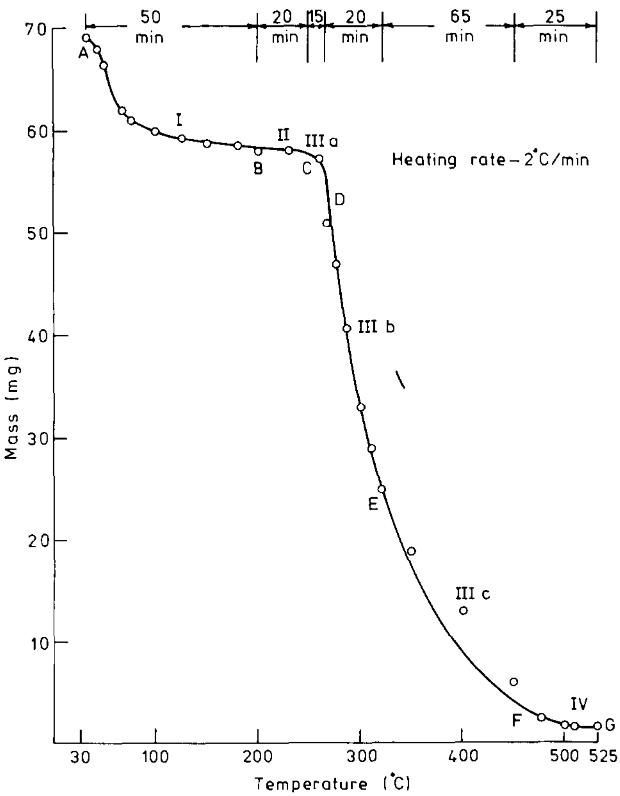

Fig. 1. TGA of untreated rice straw.

In general, there are three distinct stages which may be broadly identified as (i) removal of moisture, (ii) removal of volatile matter and (iii) combustion of fixed carbon. However, some transition and intermediate stages inbetween the above-mentioned major modes of decay can also be identified.

The results of the TGA studies of untreated rice straw and those of acid-treated rice straw are discussed separately.

TGA of untreated rice straw

As indicated in Fig. 1, the TGA records for untreated rice straw show three distinct stages, namely, drying, release of volatile matter and combustion of fixed carbon. An intermediate stage of inappreciable mass loss was

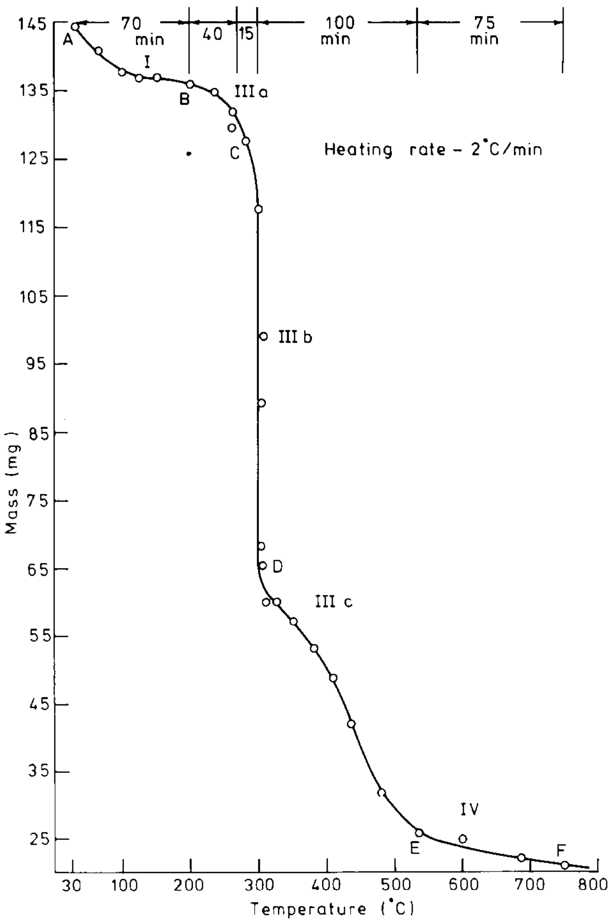

Fig. 2. TGA of rice straw, acid (1 N HCl) leached.

observed after the first stage. All the different stages of mass loss are shown in Fig. 1 as A–B, B–C, C–D, D–E, E–F and F–G. The corresponding temperature ranges were 30–200, 200–250, 250–275, 275–315, 315–475 and 475–525 °C. Stage I, indicated in Fig. 1 as A–B, is the drying stage. The temperature range of this stage was 30–200 °C and its duration was 50 min.

The second stage of mass loss, a region of inappreciable mass loss with an average temperature range of 250–275 °C, was the transition or intermediate stage. The removal of volatile matter, however, took place in the third stage. It is clear from Fig. 1 that within the temperature range 250–475 °C there are three sub-stages, indicated as IIIa, IIIb and IIIc and marked C–D, D–E and E–F respectively. Their corresponding temperature ranges were 250–275, 275–315 and 315–475 °C. The rate of volatilization was the highest in the IIIb stage. Stage IV (marked as F–G in Fig. 1) is mainly due to the combustion of carbon as a result of its oxidation.

TGA of acid-treated rice straw

The TGA curves of the various acid-leached samples were recorded to examine the effect of different chemical treatments on the thermal de-

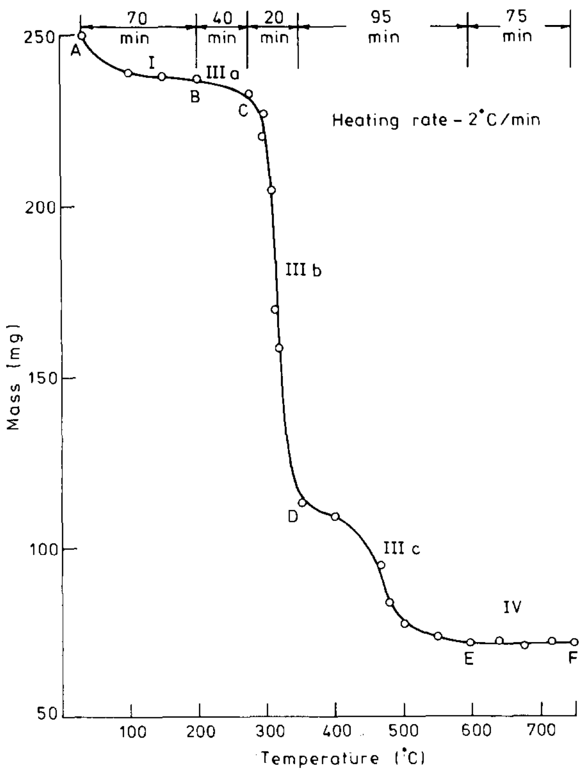

Fig. 3. TGA of rice straw, acid (6 N HCl) leached at 90 °C for 45 min.

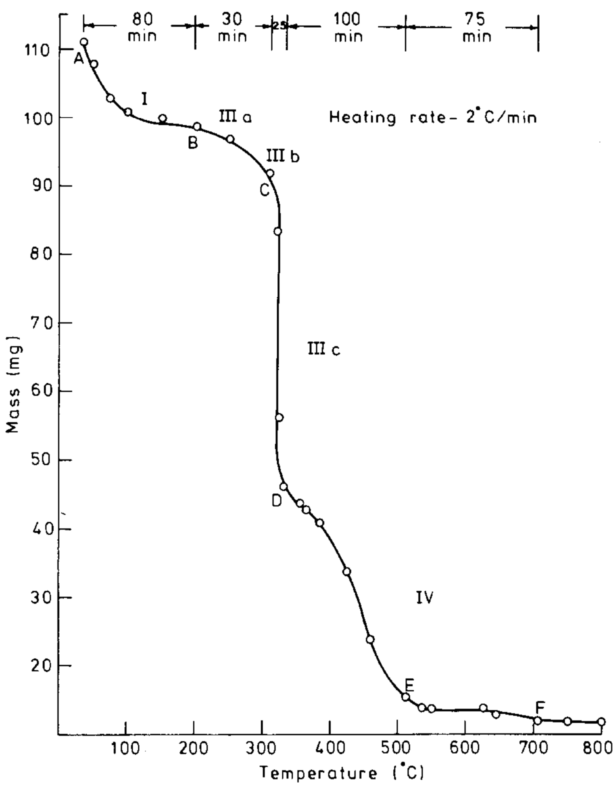

Fig. 4. TGA of rice straw, acid (1 N HNO_3) leached at 85 °C for 40 min.

composition of rice straw. Rice straw samples were treated with HCl and HNO_3 of different concentrations and digested at an elevated temperature between 80 and 90 °C for 40–50 min. In the present study the concentrations chosen were 1 N and 8 N for HNO_3 and 1 N and 6 N for HCl.

Also for acid-treated rice straw, the mass loss occurred in three distinct stages, namely, removal of moisture, release of volatile matter and combustion of the fixed carbon.

Rice straw, leached with HCl and HNO_3 exhibited slightly different TGA characteristics compared with those of untreated rice straw. There was practically no intermediate decay stage between the removal of moisture and volatile matter. It exhibited an appreciable fall in mass immediately after the completion of drying.

The TGA curves of various acid-leached rice straw samples are shown in Figs. 2–6. Stages I, IIIa, IIIb, IIIc and IV are marked in the figures as A–B, B–C, C–D, D–E and E–F. It was clear from Figs. 2–6 that the average temperature range for the removal of moisture for all acid-leached rice straw samples was 30–200 °C. The time needed for the drying operation in all cases was nearly the same.

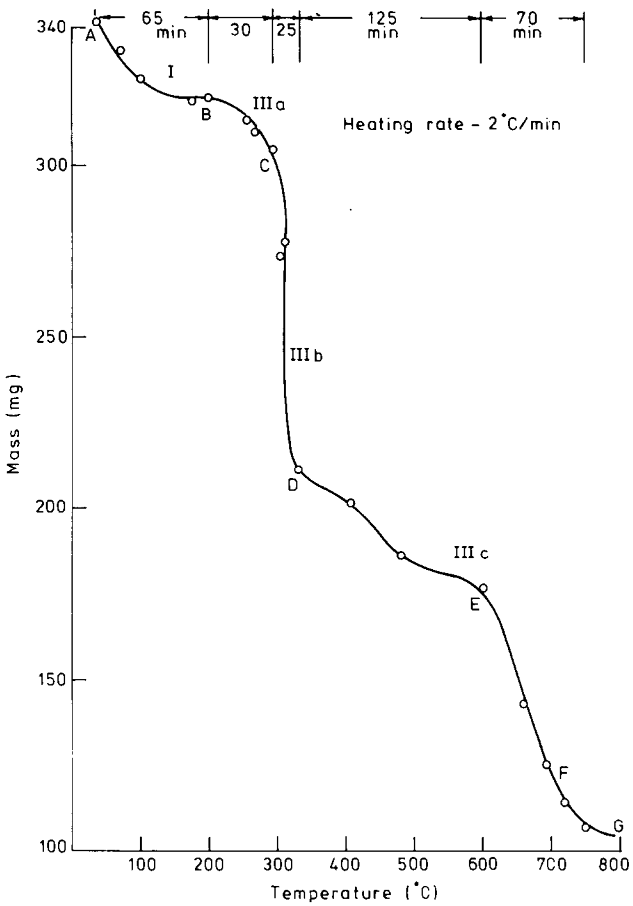

Fig. 5. TGA of rice straw, acid (8 N HNO_3) leached.

The major part of the mass loss took place as a result of the escape of volatile matter from the acid-treated rice straw. This stage can be further subdivided into three sub-stages which are indicated as IIIa, IIIb and IIIc in Figs. 2–6. The rate of mass loss is highest in the IIIb sub-stage.

It also appears from these figures that the removal of volatile matter, irrespective of all physical and chemical treatments of the rice straw, was complete at around 500 °C. The subsequent stages of combustion were due to the oxidation of the carbon in the straw.

Simultaneous TG, DTG and DTA at a heating rate of 20 °C min^{-1}

Studies of the thermal decomposition of untreated rice straw and that treated with HCl and HNO_3 of various concentrations were carried out by TG, DTG and DTA techniques.

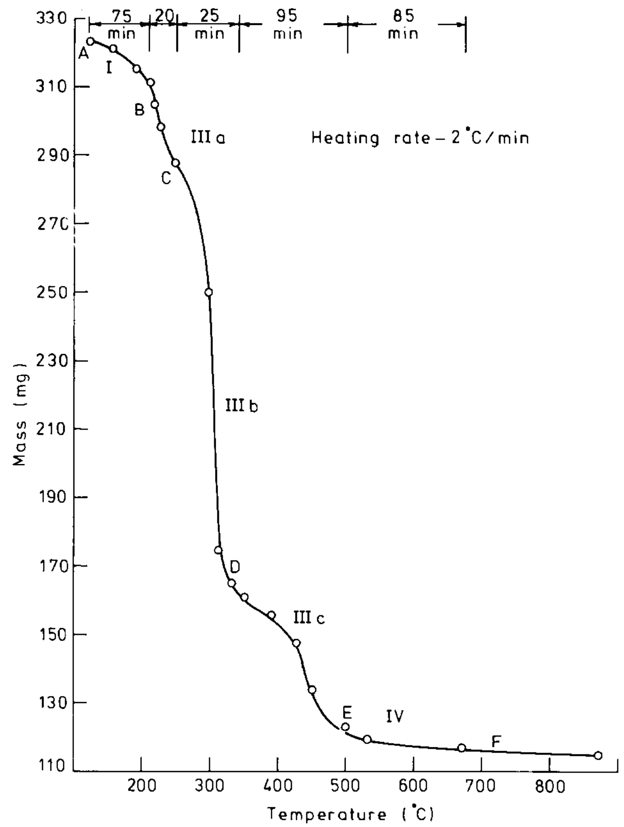

Fig. 6. TGA of rice straw, acid (1 N HCl + 1 N HNO_3) leached at 80 °C for 40 min.

The simultaneous TG, DTG and DTA curves for untreated and various acid-leached straw samples are shown in Figs. 7–12. The nature of the TG curves indicates that the loss of mass occurred in three major stages. One intermediate stage of inappreciable mass loss was also observed after the

TABLE 1

Temperature range for different stages of mass loss in the TG curves for rice straw

Treatment	Temperature range (°C)			
	Stage I	Stage II	Stage III	Stage IV
Untreated	40–200	200–275	275–350	350–550
1 N HCl	40–200	200–285	285–375	375–525
6 N HCl	40–200	200–285	285–385	385–550
1 N HNO_3	40–200	200–275	275–365	365–500
8 N HNO_3	40–200	200–275	275–390	390–565
1 N HCl + 1 N HNO_3	40–200	200–250	250–375	375–600

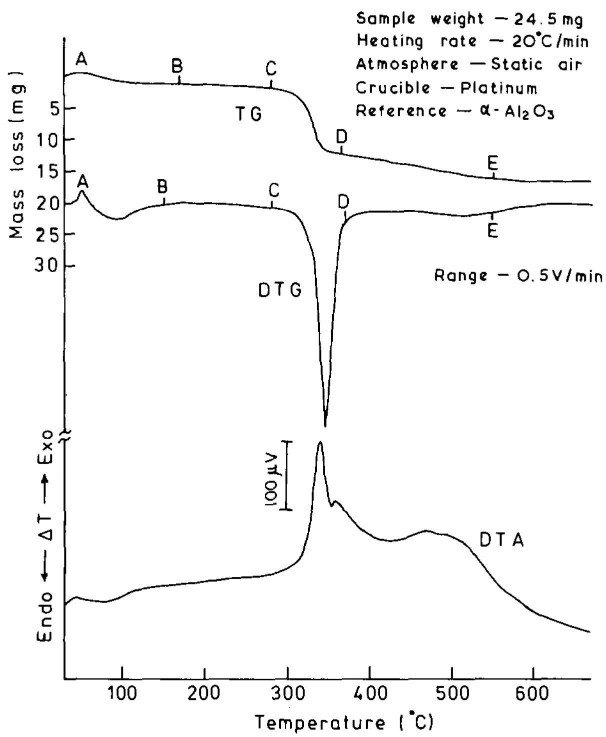

Fig. 7. TG, DTG and DTA for untreated rice straw.

first stage. The various stages of decomposition and the temperature range for each stage were identified from the trends in the TG and DTG curves. The four different stages are marked in the figures as A–B, B–C, C–D and

TABLE 2

Peak temperatures (°C) in DTG and DTA curves corresponding to different stages of mass loss in rice straw samples

Treatment	Peak temperature (°C)										
	Stage I			Stage II		Stage III			Stage IV		
	DTG	DTA		DTG	DTA	DTG	DTA		DTG	DTA	
Untreated	95	90	endo	–	–	355	340	exo	–	475	exo
1 N HCl treated	100	90	endo	–	–	345	340	exo	–	470	exo
6 N HCl treated	125	–		–	–	325	345	exo	–	465	exo
1 N HNO_3 treated	100	90	endo	–	–	330	335	exo	–	460	exo
8 N HNO_3 treated	95	95	endo	–	–	350	337.5	exo	–	470	exo

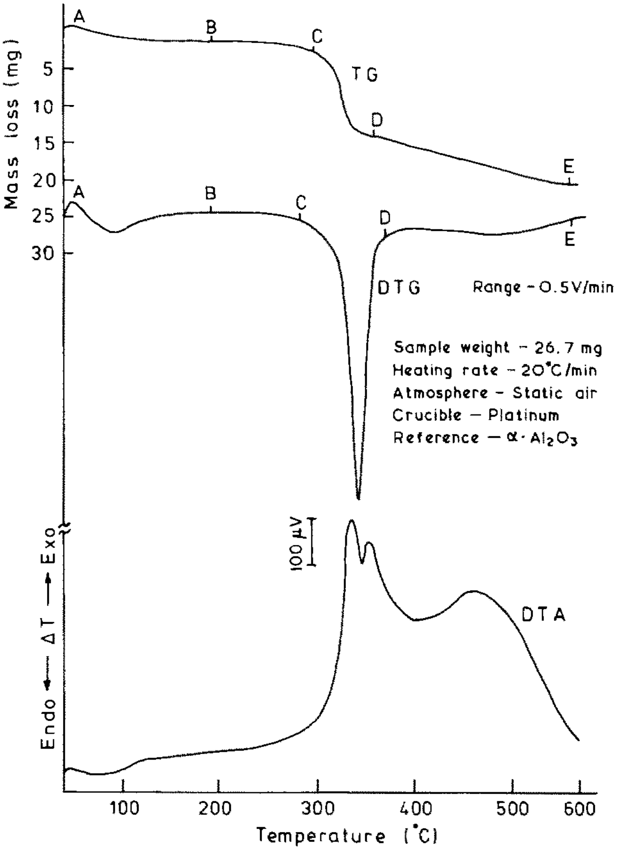

Fig. 8. TG, DTG and DTA for acid-leached (1 N HCl) rice straw at 90 °C for 50 min.

D–E. The temperature ranges are indicated in Table 1. Table 2 shows various peak temperatures in the DTG and DTA curves.

The TG curves show that the mass loss in the first stage took place in the range 40–200 °C. The DTG curves exhibit a peak in the range 95–125 °C which corresponds to the maximum rate of mass loss. The mass loss in this stage may be attributed to the removal of moisture from the material.

The second stage was identified as a plateau in the TG curves in the range 200–275 °C with an inappreciable mass loss, while the DTG and DTA curves do not show any peak in this stage. This may be considered as a transition stage.

The third stage of decomposition took place in the range 275–350 °C indicating a steep fall and a sharp peak in the TG and DTG curves respectively. The mass loss associated with this stage was due to the removal of volatile matter. The rate of mass loss for untreated straw was higher than that for treated straw. The temperature at the maximum rate of mass loss as indicated by the DTG curves was found to depend on the concentration of

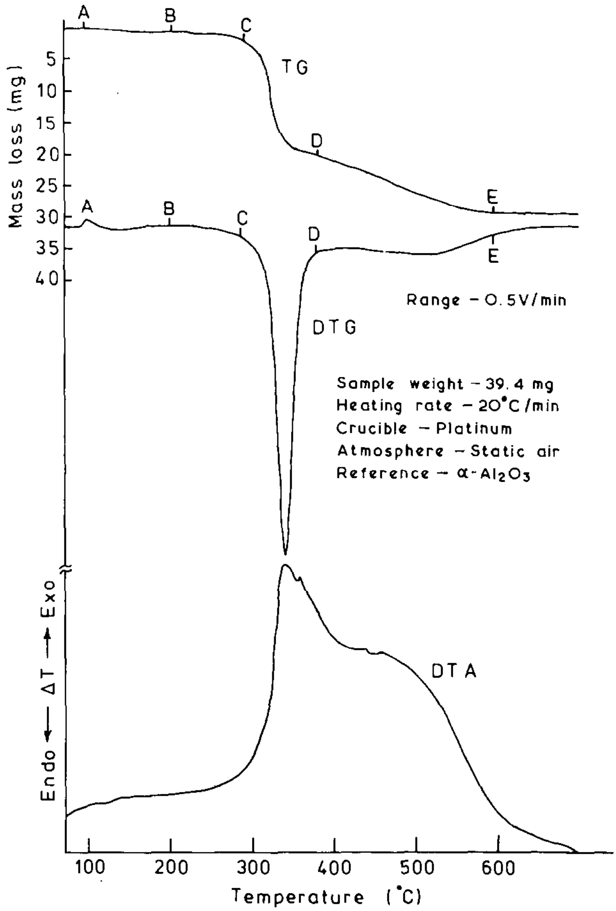

Fig. 9. TG, DTG and DTA for acid-leached (6 N HCl) rice straw at 90 °C for 45 min.

the acid used in the treatment of the straw. For untreated straw it was around 275 °C and for HCl and HNO_3 treatment it was within the ranges 250–285 °C and 250–275 °C respectively.

The fourth stage of mass loss in the range 350–600 °C corresponds to the combustion process. It is interesting to note that the final temperature in this stage is higher for untreated straw than that for the treated straw. For untreated straw it was 700 °C and for treated straw it varied from 525 °C for treatment with 1 N HCl to 550 °C for treatment with 6 N HCl, and from 600 °C for treatment with 1 N HNO_3 to 565 °C for treatment with 8 N HNO_3. This shows that treatment with acids of low concentration is desirable. The DTG curves show a gradual decrease in the rate of mass loss and the DTA curves indicate an overall exothermic reaction.

Among the four stages, the major decomposition occurred in the third and fourth stages. The temperature range of the fourth stage was higher than

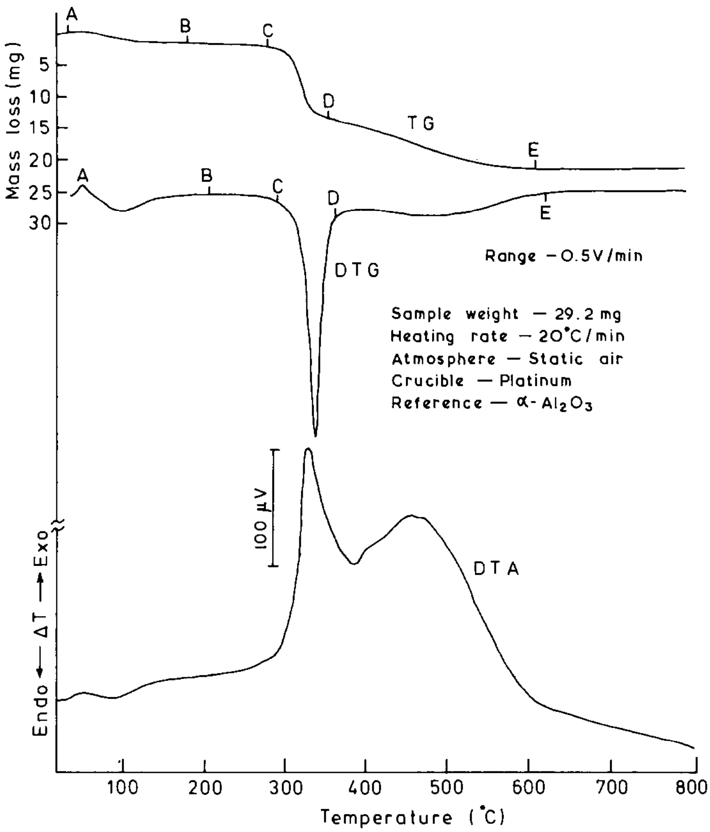

Fig. 10. TG, DTG and DTA for acid-treated (1 N HNO_3) rice straw at 85 °C for 40 min.

that of the third stage and the rate of mass loss was slower than that of the third stage. However, the rate of mass loss was the highest in the third stage.

Characterization of rice straw ash by SEM and X-ray diffraction studies

The structural characteristics of the rice straw ash obtained after combustion at 600 °C of both untreated and acid-treated straw were examined using X-ray diffraction and SEM.

A broad X-ray diffraction pattern indicated that the ashes were amorphous. It did not, however, show any sharp diffraction peak. The X-ray diffraction pattern of a typical sample is shown in Fig. 13.

The SEM studies were conducted on six typical rice straw ash samples, obtained as previously stated. The photographs in Figs. 14 and 15 also reveal the amorphous nature of the ash.

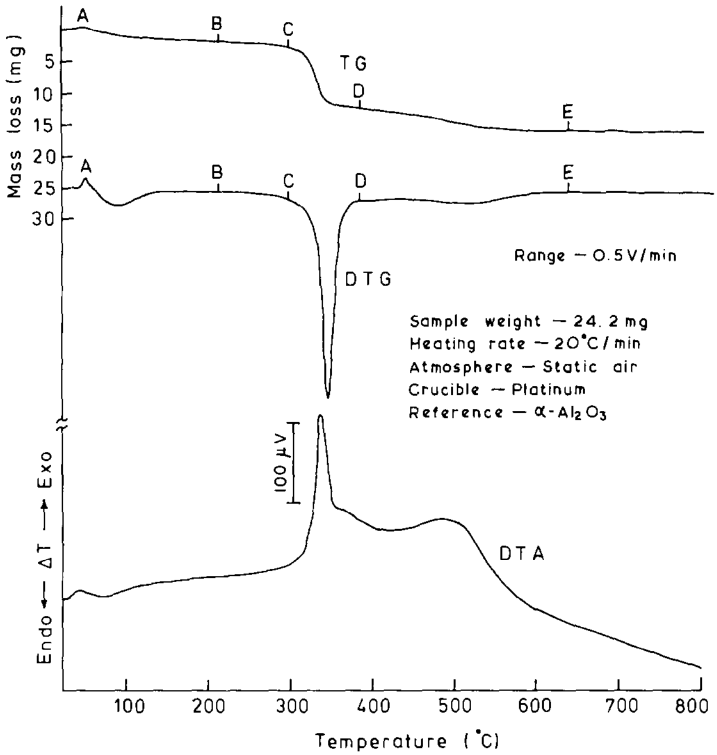

Fig. 11. TG, DTG and DTA for rice straw, acid (8 N HNO_3) leached at 85 °C for 30 min.

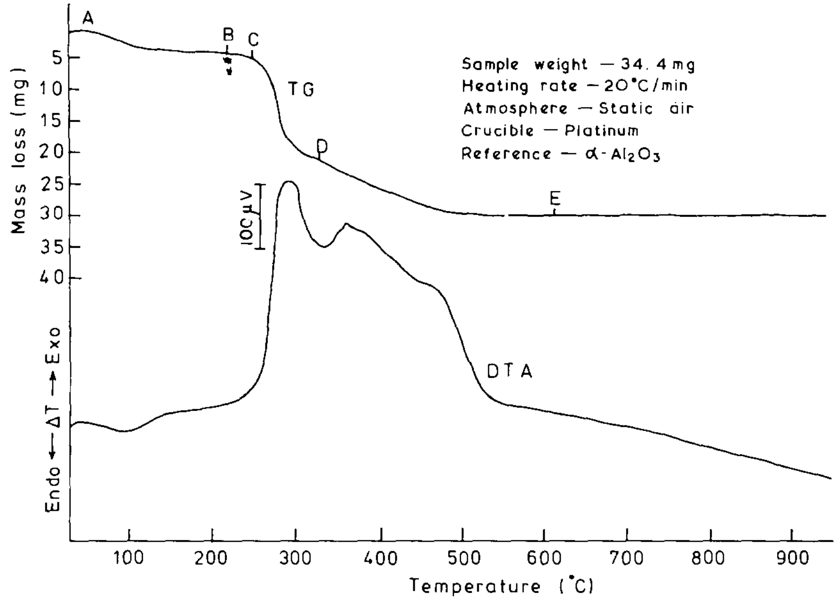

Fig. 12. TG and DTA of rice straw, acid (1 N HCl + 1 N HNO_3) leached at 80 °C for 40 min.

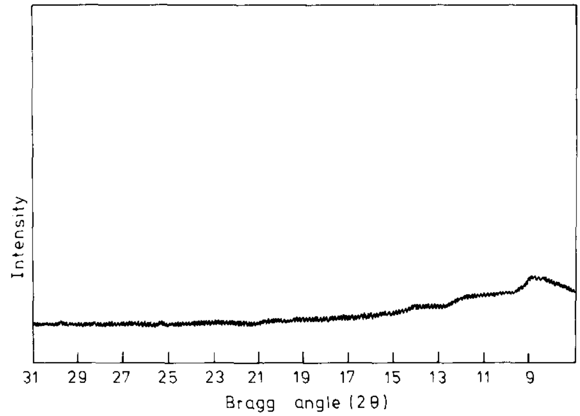

Fig. 13. X-Ray diffractogram of rice straw ash prepared at 600 ° C in the muffle furnace.

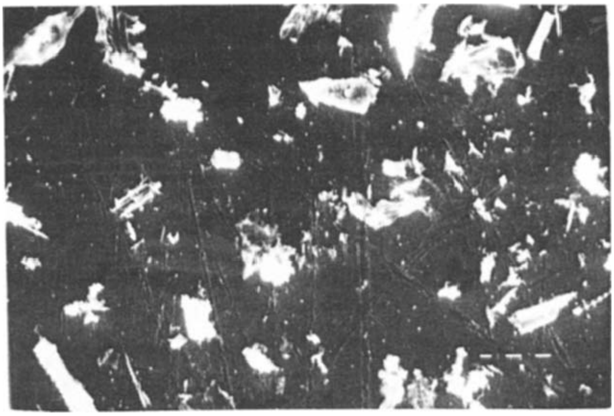

Fig. 14. SEM of rice ash obtained after burning the untreated rice straw in the muffle furnace at 600 ° C.

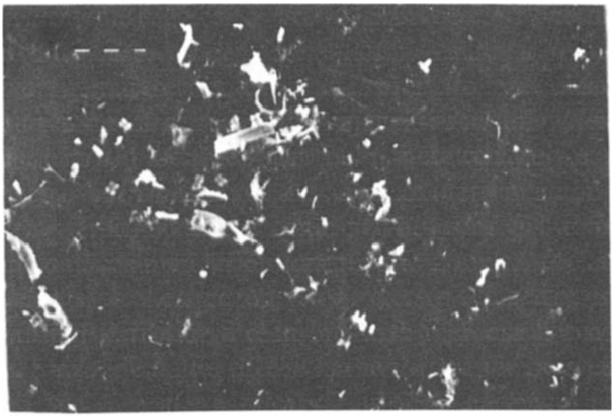

Fig. 15. SEM of rice straw ash obtained after burning the acid-leached (1 N HCl) rice straw sample in the muffle furnace at 600 ° C.

CONCLUSIONS

(1) The thermal decomposition of untreated rice straw occurs in four stages: (i) removal of moisture, (ii) intermediate stage of inappreciable mass loss, (iii) release of volatile matter and (iv) combustion of fixed carbon.

(2) The thermal decomposition of acid-treated rice straw occurs only in three distinct stages: removal of moisture, removal of volatile matter and combustion of fixed carbon. In the case of acid-treated rice straw, practically no second stage exists. Just after the drying stage, the removal of volatile matter starts taking place, which occurs in three sub-stages.

(3) Overall, the thermal decomposition of the rice straw is an exothermic process.

(4) Irrespective of any physical or chemical treatment of the rice straw, the removal of moisture, the release of volatile matter and the combustion of carbon take place at temperatures around 0–200 °C, 275–400 °C and 400–600 °C respectively.

(5) The X-ray diffractometry and SEM examination of the rice straw ash indicate that the ash obtained after thermal decomposition at temperatures up to 600 °C contains amorphous silica.

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