Study of Thermal Decomposition Process of Raw and Hydrochloric Acid Treated Rice Husk

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Abstract

The thermal decomposition process and product of raw and hydrochloric acid treated rice husk were investigated by TG, DTA, XRD and XRF. The results show that thermal decomposition process of rice husk revealed three distinct stages of mass loss, namely, removal of moisture, release of volatile matter and burning of combustible material. An exothermic reaction and endothermic peak was exhibit during the course of thermal decomposition and during the removal of moisture, respectively. The properties of rice husk ash depend on the combustion condition and the pretreated condition. Acid leaching of rice husk in dilute HCl and the appropriately combustion temperature helps in producing ash with high pure amorphous silica and completely white in color.

Key words : Rice husk, Thermal decomposition, Process, Property

Rice husk is a fibrous material with high silica content. The major constituents of rice husk are cellulose, lignin, and ash. Though the actual composition is variation with the variety climate and geographic location of growth, the following values may be considered typical : ash 20%, lignin 22%, cellulose 38%, pentosans 18%, and other organics 2%. The lignin, cellulose, and pentosans present in rice husk can be removed by controlled combustion and rice husk ash was obtained[1),2)]. The partially burnt rice husk ash contains carbon, and is therefore black in color. The fully burnt ash may be gray, purple, or white, depending on the impurities present and the burning conditions[3)]. Earlier work[4)-6)] indicates the nature of the thermal decomposition of acid-treated ground husk by using thermogravimetry. But the thermal processes and the property of rice husk ash were not reported. In view of this, the present work was undertaken with the following objectives : (1) to study the thermal decomposition process of raw and hydrochloric acid treated rice husk by thermogravimetry (TG) and differential thermal analysis (DTA) ; (2) the property of thermal decomposition product by X-ray diffraction (XRD) and X-ray fluorescence (XRF).

Received December 19, 2003

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1. Experimental sections

1.1 Materials preparation

Rice husk was supplied by the Hachinohe city, Japan. The hydrochloric acid pretreated rice husk, which is prepared by immersing rice husks in HCl aqueous solutions of different concentrations. The last husks were washed repeatedly with water until the acid was undetected in the filtrate and then air dried at room temperature.

1.2 Experimental methods

(1). thermal decomposition analysis was also performed on the DTA-TG experiment. Approximately 50 mg of sample were placed in a platinum cup for the analysis. Platinum crucibles and heat-treated α-Al_2O_3 were used as sample holders and reference sample, respectively. The curves were recorded simultaneously along with temperature rise under oxygen-free conditions. The heating rate was 10°C • min^{-1}.

(2). the properties of thermal decomposition product were conducted by XRD and XRF.

2. Results and discussion

2.1 Thermal decomposition process of raw and hydrochloric acid treated rice husk

The simultaneous TG and DTA curves for untreated and various hydrochloric acid leached rice husk samples were shown in **Figs. 1-5**. The nature of the TG curves indicated that the loss of mass occurred in three major stages. One intermediate stage of inappreciable mass loss was also observed after the first stage. This result is in good agreement with previous work[2].

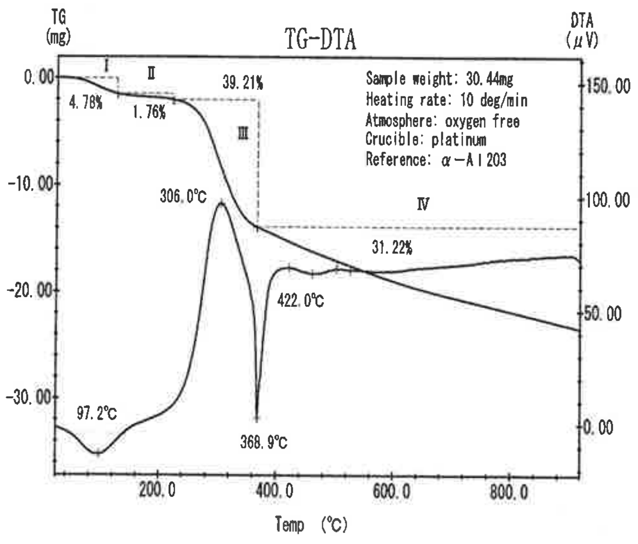

Fig. 1 TG and DTA curves for rice husk

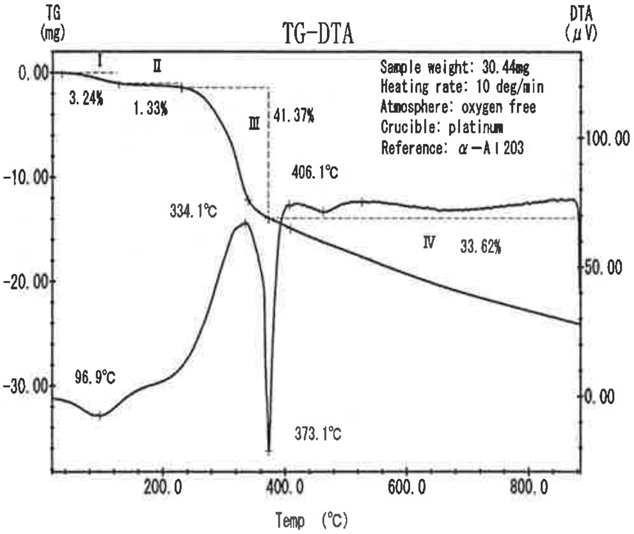

Fig. 2 TG and DTA curves for rice husk treated with 0.5N HCl at 20°C for 4 hours

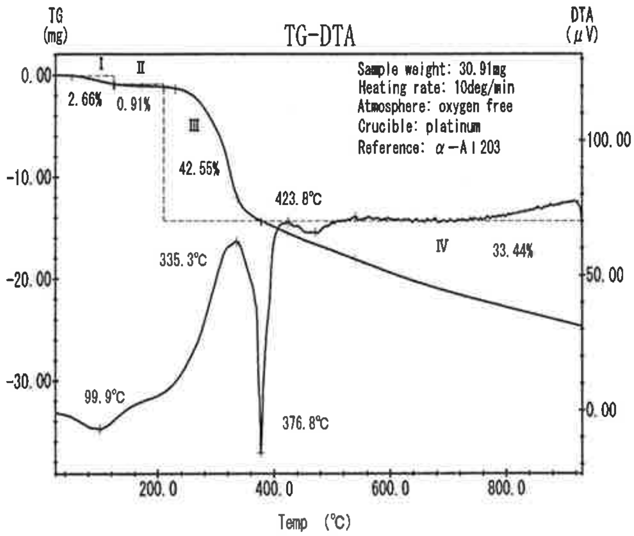

Fig. 3 TG and DTA curves for rice husk treated with 1N HCl at 20°C for 4 hours

The various stages of decomposition and the temperature range for each stage were identified from the trend of the TG and DTA curves. The four different stages are marked in the figures as I, II, III, IV. The temperature ranges were given in **Table 1**. The percentage and the mass loss in each stage as calculated from the TG curves are indicated in **Table 2**. **Table 3** shows various peak temperatures in the DAT curves.

The TG curves show that the mass loss in the first stage took place in the range 39-140°C. The DTA curves indicated an endothermic peak around which corresponds to the maximum

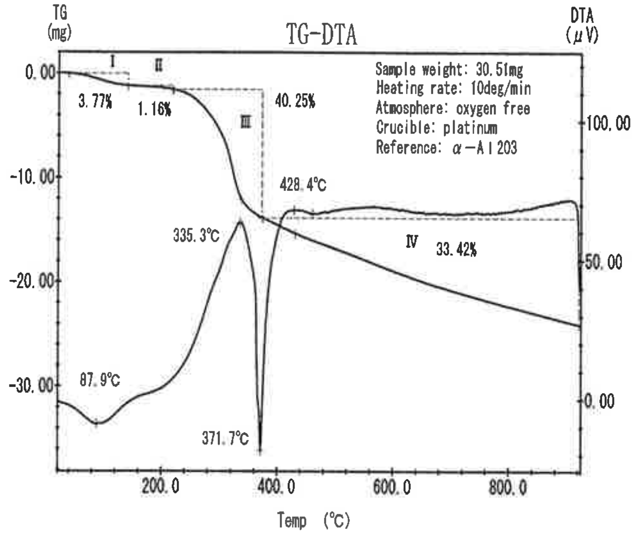

Fig. 4 TG and DTA curves for rice husk treated with 1N HCl at 20°C for 24 hours

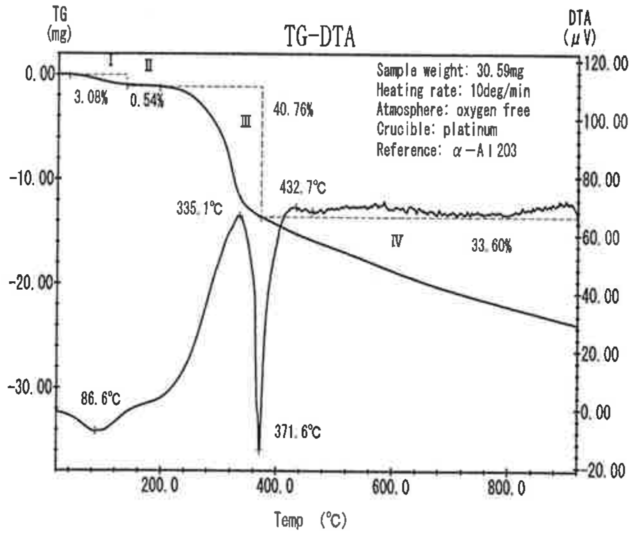

Fig. 5 TG and DTA curves for rice husk treated with 3N HCl at 20°C for 4 hours

rate of mass loss. The mass loss ranging from 2.66 to 4.78% associated in this stage may be attributed to the removal of moisture from the material. It was also reported earlier that the thermal decomposition of over dried husk was negligible below 200°C.

The second stage was identified as a plateau in the TG curves in the range 123-228°C with an inappreciable mass of 0.54-1.76%, while the DTA curves do not show any peak in this stage. This may be considered as a transition stage.

In the first and second stage the mass loss for the untreated husk was higher than that for

Table 1 Temperature range for different stage of mass loss in the TG curves

Treatment	Treatment time (hour)	Temperature range (°C)			
		Stage I	Stage II	Stage III	Stage IV
untreated sample		41-127	127-224	224-369	369-918
0.5 N HCl treated	4	41-123	123-228	228-373	373-885
1 N HCl treated	4	41-124	124-211	211-377	377-929
1 N HCl treated	24	40-140	140-219	219-372	372-920
3 N HCl treated	4	39-136	136-208	208-372	372-919

Table 2 Percentage (%) of mass loss in different stage

Treatment	Treatment time (hour)	Stage I	Stage II	Stage III	Stage IV
		Percent	Percent	Percent	Percent
untreated sample		4.78	1.76	39.21	31.22
0.5 N HCl treated	4	3.24	1.33	41.37	33.62
1 N HCl treated	4	2.66	0.91	42.55	33.44
1 N HCl treated	24	3.77	1.16	40.25	33.42
3 N HCl treated	4	3.08	0.54	40.76	33.60

Table 3 Peak temperature (°C) in DTA curves corresponding to different stages of mass loss

Treatment	Treatment time (houm)	Stage I	Stage II	Stage III	Stage IV
untreated sample		97.2 endo		306.0 exo	422.0 endo
0.5 N HCI treated	4	96.9 endo		334.1 exo	406.1 endo
1 N HCI treated	4	99.9 endo		335.3 exo	423.9 endo
1 N HCI treated	24	87.9 endo		335.3 exo	428.4 endo
3 N HCI treated	4	86.6 endo		335.1 exo	432.7 endo

endo : endothermic, exo : exothermic

the HCl treated husk, which was attributed to the dry processing to the treated husk.

The third stage of decomposition took place in the range 208-377°C indicating a steep fall in the TG curves. The mass loss associated with this stage (39.21-42.55%) may be due to the removal of volatile matter. The removal of volatile matter for untreated husk was lower than that for the treated husk. The DTA curves exhibit exothermic peaks in the rage 306.0-335.3°C. It was note that the temperature of exothermic peaks for the treated husk was higher than that for the untreated husk. For untreated husk it was 306.0°C and for HCl treatment it was within the ranges 334.1-335.3°C, respectively.

The fourth stage of mass loss (31.22-33.62%) in the range 369-929°C corresponds to the combustion process. The TG curves showed a gradual decrease in the rate of mass loss and the DTA curves indicated an exothermic reaction.

Among the four stages, the major decomposition occurred in the third and fourth stages.

Table 4 Effect of combustion temperature and pretreatment on the color of rice husk ash

Combustion temperature (°C)	Color of ash	
	unpretreated ash sample	Acid pretreatment ash sample
350	Blak	Blak
450	Gray	Blak
500	Gray	Brown
550	Gray	Brown
600	Gray	Light brown (whitish)
700	Gray	White
800	Gray	Whtie
900	Gray	White
1,000	Gray	White

The mass loss of the third stage was higher as compared to the fourth stage.

2.2 Thermal decomposition product

The color of rice husk ash is shown in **Table 4**. The color of the acid pretreated ash samples (ADR) varies from black, brown, light-brown, and white. The color of the untreated ash samples (RHA) shows the black and gray. At the lower combustion temperature, for example, below 450°C (RHA sample) and 500°C (ADR sample), the samples were black in color, it is because that these samples contained partially decomposed organic matter or unoxidized carbon. Above 550°C, the different colors of the samples are due to the metallic impurities in rice husk ash.

Table 5 shows the chemical composition of well-burnt rice husk ash obtained from the analysis by X-ray fluorescence. It indicated SiO_2 was main composition and the lower of amount of metallic impurities in the ash samples. The main metallic impurities in the ash are potassium, calcium, phosphorous, magnesium iron, and sodium. The concentration of potassium is greater than those of the other metallic elements. It can be seen that these metals including potassium are substantially reduced by treating with HCl and high pure silica was obtained.

Table 5 Chemical compositions (%) ofRHA with X-ray fluorescence analysis

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	MnO	Cl
ADR-4	98.61	0.10	0.21	0.21	<0.10	0.03	0.16	0.18	0.02	0.01
ADR-1-24	99.15	0.10	<0.10	0.21	<0.10	0.05	0.06	0.11	0.01	0.01
ADR-3-4	99.13	0.10	<0.10	0.10	<0.10	0.04	0.06	0.08	0.01	0.01
RHA55-4	94.58	0.31	0.31	0.72	0.31	0.07	2.60	0.52	0.11	0.11

Note: ADR-4(1 NHCl, 4h), ADR-1-24(1 NHCl, 24h), ADR-3-4(3 NHCl, 4h), RHA55-4, heating temperature 700°C, maintaining time 4 h

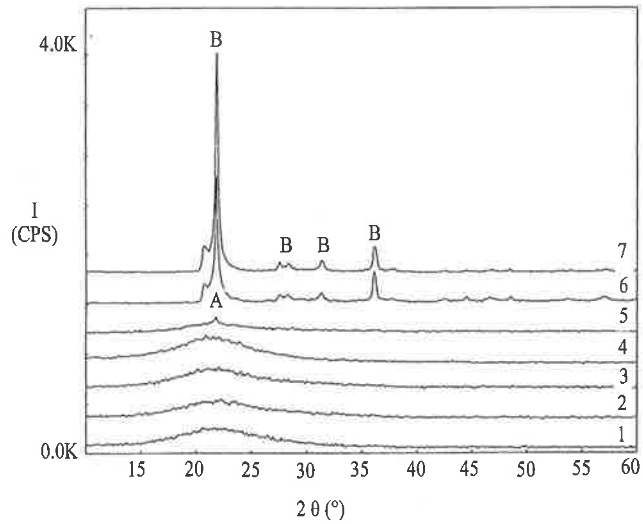

Fig. 6 XRD of RHA at different temperatures (holding time: 4 hours)
A: Distorted quartz structure B: α-Cristobalite
1. 400°C, 2. 550°C, 3. 600°C, 4. 700°C, 5. 800°C, 6. 900°C, 7. 1,000°C

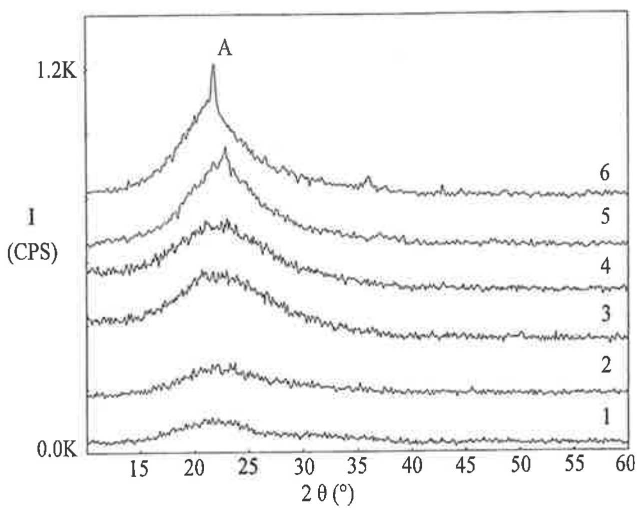

Fig. 7 XRD of ADR at different temperatures (holding time: 4 hours)
A: Distorted quartz structure
1. 600°C, 2. 700°C, 3. 800°C, 4. 900°C, 5. 1,000°C, 6. 1,100°C

The properties of rice husk ash were shown in **Fig. 6** and **Fig. 7**. All the ash samples up to RHA-700 and ADR-900 show a broad peak centered around 22.2°(2θ) on the XRD. It indicated the form of silica in rice husk ash is amorphous. The RHA sample at 800°C indicates slight crystallinity and all RHA sample after 900°C are crystalline. The crystalline phase above 800°C is identified as α-cristabalite, with a trace of tridymite. On the other hand, The

ADR sample at 1,000°C and above indicate a slight crystallinity. The phase is identified as a crystalline phase of distorted quartz structure, caused by lattice disorder. The results show that hydrochloric acid treatment of rice husks inhibits the growth of the crystallize phase from amorphous silica in rice husk ash. It also shows that widening the ashing temperature range is beneficial to the industrial production. To our knowledge, this finding has not been reported previously in the literature.

4. Conclusions

Within the limits of the present studies the following conclusions can be drawn.

1) Thermal decomposition process of rice husk revealed three distinct stages of mass loss, namely, removal of moisture, release of volatile matter and burning of combustible material. The major decomposition occurred in the release of volatile matter and burning of combustible material.
2) The DTA records exhibit an exothermic reaction during the course of thermal decomposition and endothermic peak during the removal of moisture.
3) The properties of rice husk ash depend on the combustion condition and the pretreated condition. Acid leaching of rice husk in dilute HCl and the appropriately combustion temperature help in producing ash with high pure amorphous silica and completely white in color.

References

1) Houston, D.F., "Rice hulls", Rice chemistry and Technology (Editor : D.F. Houston), American Association of cereal chemistry, St. Paul, Minnesota, 1972, 301-352.
2) C. real, M.D. Alcala, J.M. Criado, Preparation of silica form rice husks, Journal of the American Ceramic Society, 79, (1996) 2012-2016.
3) Qingge Feng, Shuichi Sugita, ect., Thermal decomposition of hydrochloric acid treated rice husk and properties of its product, Journal of the Society of Inorganic Materials, 9, (2002) 505-510.
4) A. Chakraverty, P. Mishra, H.D. Banerjee, Investigation of combustion of raw and acid-leached rice hush for production of pure amorphous white silica. Journal of materials science, 23, (1988) 21-24.
5) A. Chakraverty, P. Mishra, and H.D. Banerjee, Investigation of thermal decomposition of rice husk. Thermochim. Acta., 94, (1985) 267-275.
6) Jose James and M. Subba Rao, Silica from rice husk through thermal decomposition, Thermochim. Acta., 97, (1985) 329-336.