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EFFECT OF THE COMBUSTION PROCESS ON THE STRUCTURE OF RICE HULL SILICA

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ABSTRACT

The study was carried to clarify the effect of thermal decomposition of rice hulls on the amorphous structure of silica ash. The ash obtained by thermal decomposition of hulls at temperatures in the range 500—1150°C for one hour was evaluated by X-ray diffraction. The ash prepared at comparatively lower temperatures (500—600°C) still consists of amorphous silica. Cristobalite was detected at 800°C. At 1150°C, both cristobalite and tridymite were present.

The ash produced by combustion of rice hulls in a fixed bed at different air rates was evaluated. The amorphous structure of silica was present in the case of combustion at low air rates. At comparatively higher air rates, crystallization of silica takes place. The results obtained clarify the optimum conditions for production of amorphous silica by combustion of rice hulls in fixed beds.

INTRODUCTION

Rice hulls are the largest by-product of rice milling and their commercial utilization could have a major impact upon the economics of rice milling and consequently upon the economics of developing countries. Of the various applications of rice hulls, this investigation aims to optimize their thermal decomposition to obtain an industrially usable ash or intermediate for the synthesis of other products. The incineration of the organic components of rice hulls causes a high percentage of small pores in the ash skeleton. This highly porous ash is a favourable raw material for the production of thermally insulating refractories [1]. The rice hull ash is characterized by high melting point, high porosity, high specific surface, high reactivity during changes in structure and chemical reactions of the silica and low iron content. These properties make the ash a valuable raw material for many industries.

For this study, rice hulls from Rashid Rice Mills in Egypt were used. The average chemical composition of rice hulls is 37.7% C, 5.2% H_2, 36.6% O_2, 0.5% N_2, 20% ash. The average silica content of the ash was about 94%. The remaining constituents consist mainly of K_2O, Na_2O, CaO, and MgO.

The structure of silica ash obtained under different conditions was evaluated by X-ray diffraction analysis.

The study aims to clarify the optimum conditions for obtaining amorphous silica by combustion of rice hulls in fixed beds.

EXPERIMENTAL

Preparation of rice hull ash

Rice hull ash was prepared at different temperatures. The samples were prepared from raw rice hulls by heating in a laboratory muffle furnace. The temperature was increased gradually during about 40 min to the required temperature. Then the maximum temperature was maintained for one hour, after which the ash was quenched in air.

Combustion of rice hulls in a fixed bed

Two combustion units were used to clarify the effect of the combustion system on the structure of rice hull silica. The units used were of the fixed bed type, the smaller having a volume of 0.1 m^3 and the larger 1.5 m^3. The combustion process was carried out at different air flow rates. The attained temperatures of combustion were functions of the rate of combustion and heat losses in the unit. However, in some experiments, additional heat was added to increase the temperature of combustion.

X-Ray diffraction analysis

X-Ray diffraction analysis was carried out using a Philips X-ray diffractometer. The ground samples were analyzed by CuK_α radiation at 1.54 Å. The scanning rate was 2° C min^{-1}.

RESULTS AND DISCUSSION

Effect of thermal treatment on the structure of rice hull silica

The ash samples prepared at different temperatures in the muffle furnace were analysed by the X-ray diffraction method. The diffraction patterns are given in Fig. 1. Raw rice hulls without any thermal treatment were also analyzed. Curve 1 represents the X-ray diffraction of the raw hulls. A diffused peak at about $\theta = 22°$ was noticed, indicating the presence of amorphous silica (disordered cristobalite). Curve 2 represents the X-ray diffraction of hulls ash prepared at 500° C for one hour. As seen from the curve, the diffused peak remains at about $\theta = 22°$, indicating the presence of amorphous silica. No sharp peaks were noticed at this temperature, indicating the

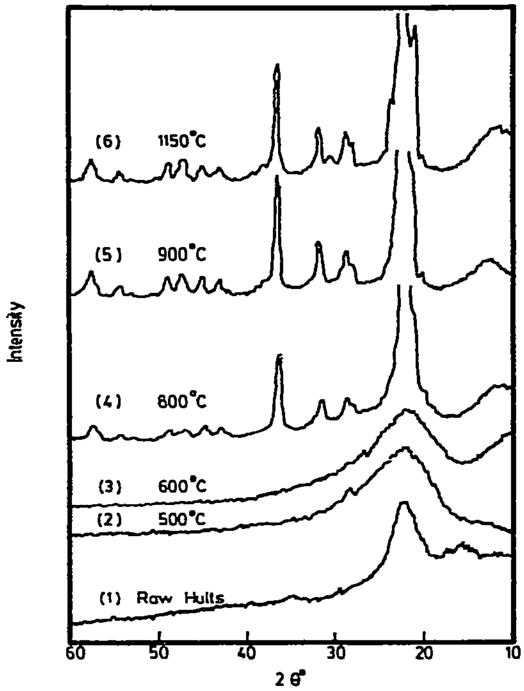

Fig. 1. X-Ray diffraction patterns of rice hull ash prepared at different temperatures.

absence of a crystalline phase. The same results were obtained for the rice hull ash prepared at 600° C for one hour (curve 3). Crystallization of silica ash was observed at 800° C as shown by the sharp peaks in curve 4, indicating the crystallization of cristobalite. These results agree with those obtained by Bartha and Huppertz [1]. They mentioned that the crystallization of silica ash begins at a temperature of 725° C in the case where hulls were heated for one hour.

At higher temperatures (900—1150° C), more sharp peaks were noticed (curves 5, 6) indicating the formation of different crystalline forms of silica. Thus at 900° C (curve 5), only cristobalite was detected, while at 1150° C (curve 6), both cristobalite and tridymite were present. This is in agreement with the findings of many investigators [2,3]. Thus Houston [2] reported that cristobalite, when heated to 900—1400° C, tends to convert to tridymite. Jones [3] reported that rice hull ash obtained at high temperatures consists essentially of tridymite and cristobalite.

Austrheim [4] reported that the amorphous silica collected from the smoke of silicon metal furnaces exists in the amorphous state at temperatures lower than 1050° C, which is much higher than the temperature of crystallization of cristobalite obtained in our study and also that of Bartha [1]. The deviation may be due to the high purity of the silica used in Austrheim's study [4] compared with rice hull ash which contains about 6% fluxing impurities. However, Austrheim [4] mentioned that the transformation of cristobalite to tridymite was optimum at 1200° C, which is in agreement with our findings.

Therefore, it can be concluded that at temperatures below 600° C, the rice hull silica still exists in the amorphous state (disordered cristobalite). At higher temperatures (800° C), crystallization of cristobalite takes place. Transformation of cristobalite to tridymite started at 1150° C.

Effect of fixed bed combustion on the structure of rice hull silica

The state of the ash prepared in a laboratory muffle furnace was compared with that of the ash produced in the fixed bed pilot units. The effect of the air flow rate during the combustion process, the size of the combustion unit and the heating effect were studied.

Effect of air rate

Small combustion unit. X-Ray diffraction patterns of the ash produced in the small fixed bed combustion unit are given in Fig. 2. Curve 1 illustrates the X-ray diffraction pattern of the ash produced at an air flow rate of 1.77 m^3 $(m^2\ h)^{-1}$. A diffused peak at about $\theta = 22°$ was noticed, indicating the presence of amorphous silica. No sharp peaks were observed, indicating the absence of any crystalline state of silica. The same results were obtained for combustion at an air flow rate of 3.62 m^3 $(m^2h)^{-1}$ (curve 2). Curves 1 and 2 are similar to the X-ray diffraction curves obtained for the ashes prepared at 500 and 600° C (Fig. 1).

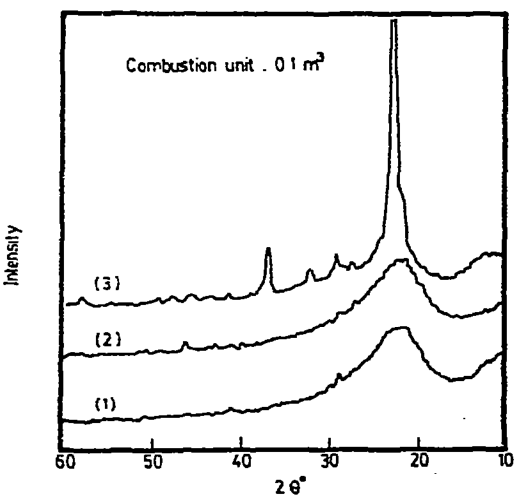

Fig. 2. X-Ray diffraction patterns of rice hull ash obtained at different air flow rates. (1) 1.77; (2) 3.62; (3) 6.19 m^3 $(m^2\ h)^{-1}$.

Curve 3 illustrates the X-ray diffraction patterns for the ash produced by combustion of rice hulls at an air flow rate of 6.19 m^3 $(m^2\ h)^{-1}$. Sharp peaks were noticed indicating the presence of crystalline cristobalite. Comparing curve 3 with the reference curve of Fig. 1, it can be observed that the curve is similar to curve 4 for the ash prepared at 800°C. The measured combustion temperatures in the bed centre were near to this temperature, indicating the main effect of temperature on the crystallization of silica.

Large combustion unit. Figure 3 illustrates the effect of air rate on the state of silica produced in the large combustion unit. The X-ray diffraction patterns are given for the ash produced at different air flow rates in the range 0.55—1.98 m^3 $(m^2\ h)^{-1}$. The difussed peak at about $\theta = 22°$ was noticed for all curves of these flow rates. However, a sharp peak was noticed for the ash produced at a rate of 1.98 m^3 $(m^2\ h)^{-1}$, indicating the beginning of crystallization of the silica (curve 5). The obtained peaks indicate the formation of α quartz. The temperature of combustion was 675°C for the given air rate. A difference was noticed by comparing curve 5 of Fig. 3 with the reference X-ray diffraction curve of Fig. 1. Crystallization started at lower temperatures than those of ash heated for one hour. The difference may be attributed to the comparatively longer duration of heat treatment in the case of ash produced in fixed bed combustion.

The ash produced at air flow rates in the range 0.55—0.8 m^3 $(m^2\ h)^{-1}$ still consists mainly of amorphous silica. The observed temperatures of combustion for these air rates were in the range 385—505°C.

Comparing the X-ray diffraction curves of the ashes produced in the large combustion unit with those obtained in the small unit, a great difference was

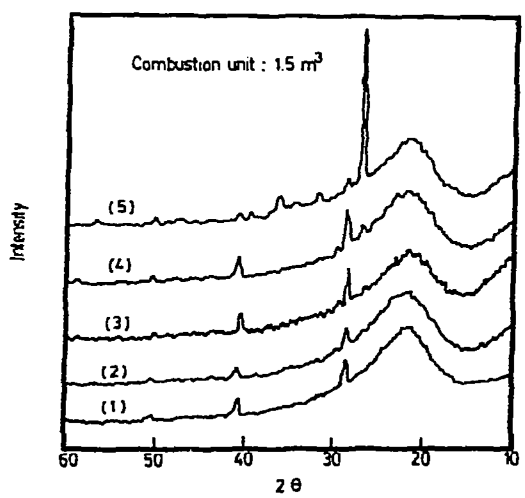

Fig. 3. X-Ray diffraction patterns of rice hull ash obtained at different air flow rates. (1) 0.55; (2) 0.55; (3) 0.666; (4) 0.8; (5) 1.98 m^3 $(m^2\ h)^{-1}$.

noticed. Thus, while crystallization of silica begins at an air flow rate of 1.98 m^3 $(m^2 h)^{-1}$ (formation of α quartz) for the ash produced in the large combustion unit, only amorphous silica was obtained for about double this rate [3.62 m^3 $(m^2 h)^{-1}$] in the small combustion unit. The deviation may be due to the difference in temperatures of combustion obtained in the two units as a result of the difference in heat losses. If the X-ray diffraction curves for both units are compared based on the actual temperature of combustion, the deviation is not great.

Effect of external heating

The effect of external heating during the combustion process on the structure of rice hull silica is shown in Fig. 4. X-Ray diffraction patterns are given for different cases of combustion. The air rate was nearly constant in the range 1.77—2.36 m^3 $(m^2 h)^{-1}$. Curve 1 illustrates the X-ray diffraction patterns for self-combustion without external heating. Curve 2 shows the X-ray diffraction patterns for combustion with additional alternating heating at the bed bottom, while curve 3 shows that of combustion with continuous addition of heat. As seen from Fig. 4, curve 1 indicates the absence of crystalline silica. Sharp peaks were noticed for curve 2 in the case of alternating heating and which becomes sharper in the case of continuous heating during the combustion process (curve 3), indicating the formation of cristobalite. Thus, external heating during the combustion process raises the temperature of combustion and accordingly assists the crystallization of silica.

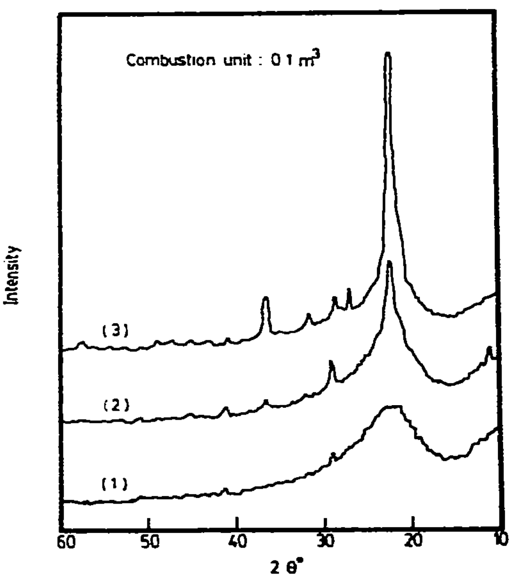

Fig. 4. X-Ray diffraction patterns of rice hull ash obtained by combustion with additional heating. (1) Air flow rate 1.77 m^3 $(m^2 h)^{-1}$, no external heating; (2) air flow rate 2.26 m^3 $(m^2 h)^{-1}$, alternating external heating; (3) air flow rate 2.36 m^3 $(m^2 h^{-1})$, external heating.

CONCLUSIONS

Silica in raw rice hulls is present in the amorphous state. The ash obtained by thermal decomposition of rice hulls at temperatures in the range 500—1150°C for one hour was evaluated by X-ray diffraction. The ash prepared at lower temperatures (500—600°C) still consists of amorphous silica. At 800°C, cristobalite was detected while at 1150°C, both cristobalite and tridymite were present.

The effect of air flow rate on the structure of rice hull silica in case of combustion in a fixed bed was clarified. At lower air rates, amorphous silica still exists, but at moderate combustion rates, quartz was detected. At comparatively higher air rates, crystallization of cristobalite takes place.

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