

Studies on the formation of black particles in rice husk silica ash

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Abstract

The formation of black (carbon fixed) particles in rice husk silica ash has been studied in detail. The formation of black particles in the silica obtained by calcination of raw untreated rice husks, is higher than that in acid treated rice husks. The tendency to form black particles increases with increase in the heating rate and the temperature of calcination of the untreated rice husks. Potassium has been shown to cause the formation of black particles in rice husk silica. By treating with 3.0 N HCl acid the formation of black particles can be avoided. There is no effect of heating rate on the formation of black particles in silica from acid treated rice husks. Treatment with HCl acid was found to decrease the oxidation (burning) of carbon at lower temperature (400°C). © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The presence of silica in rice husk (RH) has been known since 1938.¹ Rice husks produce a high ash content, varying from 13 to 29 wt.% depending on the variety, climate, and geographic location. The ash is largely composed of silica (87–97%) with small amounts of inorganic salts.² Due to its high silica content RH has become a source for preparation of a number of silicon compounds such as silicon carbide,^{3,4} silicon nitride,⁵ sialon, zeolite.⁶ Silica ash obtained by calcining RH is also used in the cement industry. RH silica has fine particle size and high reactivity and has been used in the production of activated silica, sodium silicate, potassium silicate and solar grade silicon.⁷

Though the ash of RH is rich in silica, the raw RH contains mainly organic matter ($\cong 85\%$) composed of cellulose, lignin, D-xylose, small quantities of methyl glucuronic acid and D-galactose. The elemental analysis of the organic matter as calculated by Sharma et al. is 51 wt.% carbon, 7 wt.% hydrogen and 42 wt.% oxygen.⁸ Unless the gasses and vapours evolved during the coking or calcining process are used for heating purposes, the waste of heat energy is two fold. Instead of utilising the

heat energy in the RHs (3000 Kcal/kg),⁹ heat is applied to RHs during coking or calcining. The RH as an agricultural waste has been used as a heat source for firing bricks and tiles in kilns and for domestic heating. Large quantities of RH ashes are available from such kilns.

The burning of RH in air always leads to the formation of silica ash varying in colour from grey to black and of inorganic impurities along with unburned carbon. An attempt to remove the unburned carbon by further heating to higher temperatures ($> 700^\circ\text{C}$) leads to the crystallisation of amorphous silica to cristobalite and tridymite.¹⁰ The unburned carbon in the black particles cannot be removed by oxidation as it is fixed with silica. In this work an attempt is made to understand the formation of the black particles in silica ash from rice husks.

2. Experimental procedure

Dry raw RHs (RRH) were sieved to eliminate residual rice and clay particles. They contained 81.52 wt.% of organic material and 18.48 wt.% of ash (silica). The RRH were subjected to acid treatment. A 200 g sample of RRH was fed into 3 N HCl solution in deionised water, and boiled for 1 h. After thorough washing with deionised water, the RRH were filtered and dried in an oven at 110°C. These acid treated RHs were designated as TRH1. Another 200 g sample of RRH was treated

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similarly with 5.6 N HCl solution. The RRH treated with 5.6 N HCl solution are designated as TRH2. Twenty gram samples of RRH, TRH1 and TRH2 were placed in separate rectangular stainless steel trays of length 15 cm, breadth 10 cm, and height 2.5 cm and introduced into a muffle furnace where calcination was conducted at 400, 500, 600, and 700°C. Two sets of experiments were conducted. In the case of slow heating, the RH samples were loaded into the furnace at room temperature. The rate of heating employed was 5°C/min. The samples were held at the calcining temperature for 4 h. At 720°C the samples were held for 2 h only.

In the case of sudden heating the trays containing the RH samples were loaded into the furnace at the required calcining temperature (400, 500, 600 and 700°C). At 700 and 600°C the soaking was carried out for 3 h. At 500 and 400°C the duration of soaking was 4 h. When the RHs were suddenly put into the furnace, they caught fire and burned immediately with a rise in furnace temperature to 750±20°C. After the disappearance of the flame, further decarbonisation took place.

The acid treated and untreated RHs, and the silica ashes obtained were analysed by X-ray diffractometry (XRD), scanning electron microscopy (SEM) and chemical analysis. In the case of RRH and TRH1 the husks were compacted in a steel die to make samples for XRD analysis. All other samples for XRD analysis were in powder form. A Philips X-ray diffractometer, model PW1840 with CuK radiation through Ni filter was used. An SEM of International Scientific Instruments, model ISI-100A, was used to study the morphology. The silica ash was analysed by a Varian model AA-5, atomic absorption spectroscope (AAS). To stabilize the weights, the samples of silica ash were first heated in air at 1000°C for 3 h. The weight loss due to the removal of moisture and adsorbed gases was determined. Then they were treated with HF+H₂SO₄, dried and heated at 1000°C for 1 h to remove SiO₂. Further, the samples were dissolved in 5.0 N HCl to make solutions for AAS analysis. The weight of the black residue was taken to represent the unburned fixed carbon.

3. Results

After treatment with 3 N HCl the appearance of TRH1 [Fig. 1(b)] is not much different from that of RRH [Fig. 1(a)]. The silica is present all over the rice husk but is concentrated in protuberances and hairs (trichomes) on the outer epidermis, and also in the inner epidermis (adjacent to the rice kernel).¹¹ The remaining areas lean in silica or rich in organic matter were attacked. Slight smoothing around the protuberances and trichomes, and widening of parallel grooves between the protuberances can be seen. But after treatment with 5.6 N HCl the TRH2 appeared like charred

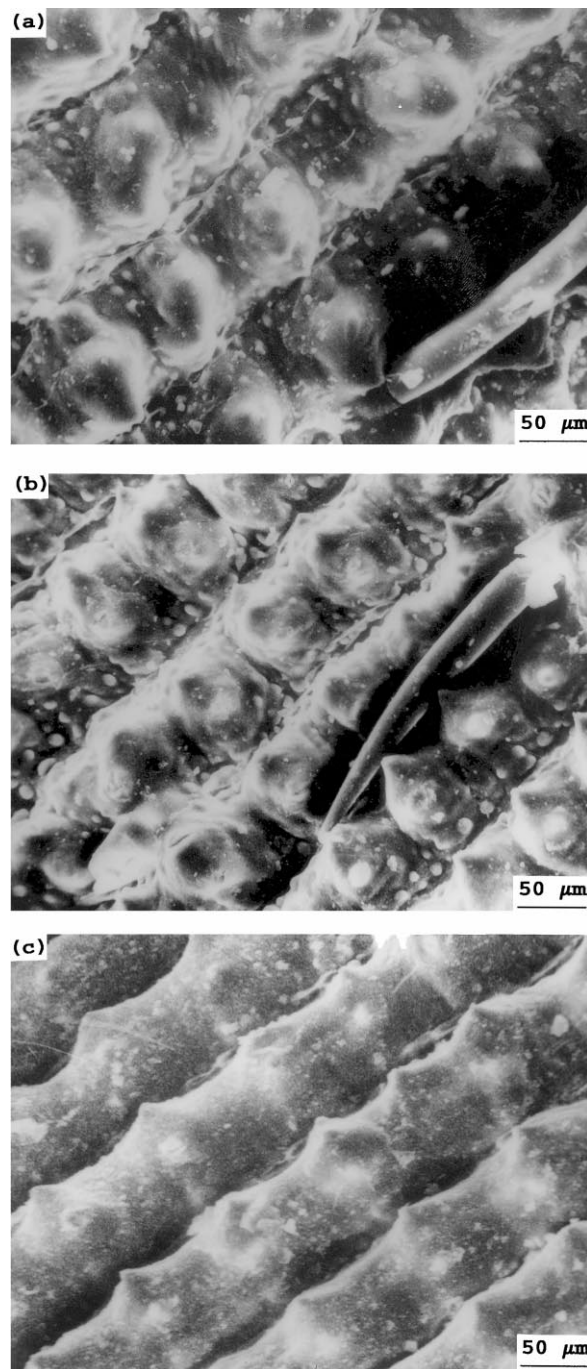


Fig. 1. SEM micrographs of outer epidermis of (a) RRH, (b) TRH1 and (c) TRH2.

RHs with a fragile nature [Fig. 1(c)]. From smoothing of the surfaces and relative shrinking, the areas leached out due to chemical burning can be seen. The extent of attack of HCl acid on organic matter in RH can be seen in Fig. 1(c). The protuberances and trichomes (horns) rich in silica¹¹ are not affected.

The appearance of ashes (silica) obtained from different samples is shown in Fig. 2. Upon slow heating the RRH has yielded silica slightly grey in colour. The brightness increased with increase in temperature of calcination.

But rapid or sudden heating resulted in the formation of black (carbon fixed) particles. The extent of black particles increased with increase in temperature of calcination. At lower temperatures (400, 500°C), TRH1 and TRH2 yielded charred RHs. With increase in calcination temperature the whiteness increased. At 700°C, the acid treated RHs (TRH1 and TRH2) yielded bright white silica. There is no considerable affect of heating rate on the formation of white ash from TRH1 and TRH2.

There is no difference in XRD patterns of RRH, TRH1, and TRH2. All three samples yielded amorphous patterns (Fig. 3). The XRD patterns of silica obtained by slow heating to 700°C, are shown in Fig. 4. Silica in all the three samples is in an amorphous state. However, in RRH a small peak corresponding to carbon is noticed. Upon sudden heating the intensity of this peak increased (Fig. 5). To examine this aspect the black particles obtained upon sudden heating of RRH at 700°C were collected separately and analysed through XRD. The peak of carbon is more prominent in this sample [Fig. 5(c)].

The impurity analysis of RH silica ashes obtained at 700°C is given in Table 1. The level of impurities decreased considerably after acid treatment. The loss in weight by heating at 1000°C/3 h is high in TRH1 and

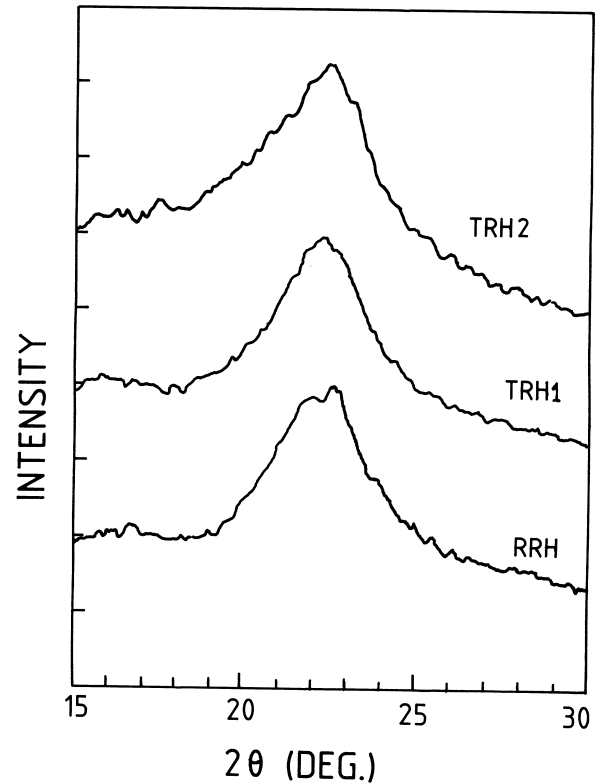


Fig. 3. XRD patterns of RRH, TRH1 and TRH2.



Fig. 2. The appearance of silica ashes obtained after calcining at different temperatures.

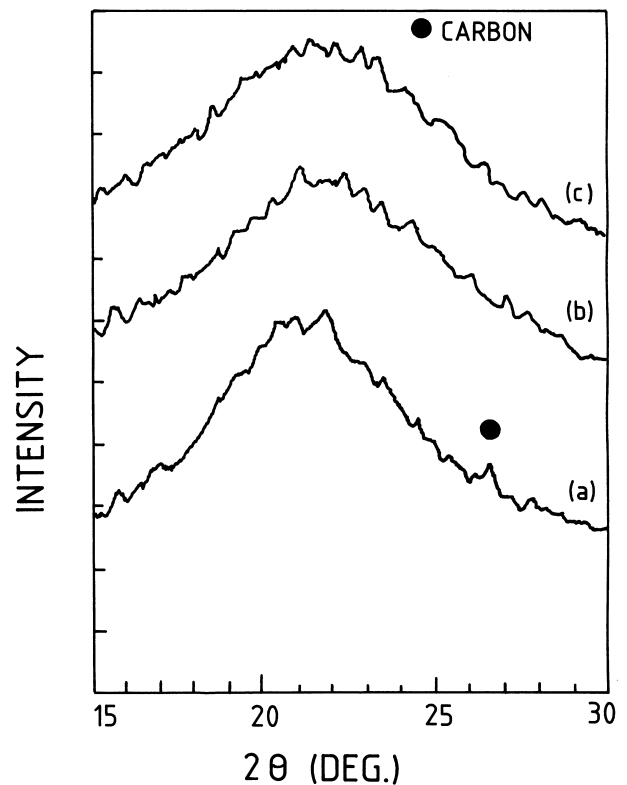


Fig. 4. XRD patterns of silica ashes obtained by slow heating at 700°C. (a) RRH, (b) TRH1 and (c) TRH2.

TRH2. But the corresponding carbon residue is very low. Similarly in the RRH slow heated sample, the loss in weight after heating at 1000°C is more than that in RRH suddenly heated sample. The highest quantity of carbon residue was observed in RRH suddenly heated sample.

4. Discussion

When RHs are subjected to acid treatment, the cellulose which forms the main body of raw RH is reduced and carbohydrate is blackened due to the removal of oxygen. The proteins in the RHs are decomposed into

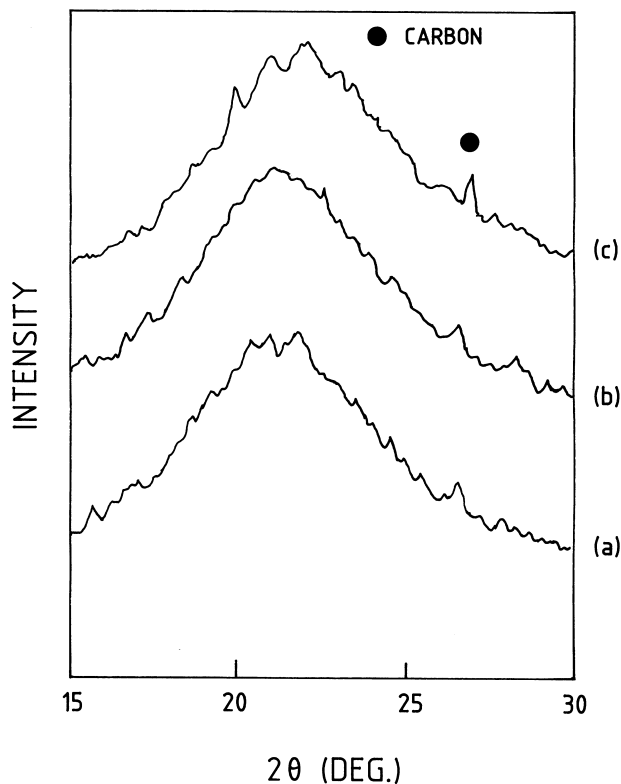


Fig. 5. XRD patterns of (a) RRH, and silica ashes obtained from RRH (b) by slow heating and (c) by sudden heating at 700°C.

amino acids, and the cellulose of larger molecular weight is leached out as smaller molecular weight compounds.¹² From the chemical analysis (Table 1), we can notice that the impurities in RH are substantially removed by acid treatment. The major impurity in RRH is potassium. The potassium must be accelerating the carbon fixation in RH ash. Potassium oxide (K_2O) which dissociates upon heating at 620 K forms elemental potassium whose melting point is 336.8 K. Potassium (K) in the RH causes surface melting and accelerates the crystallisation of amorphous silica to form cristobalite.¹³ Hanafi et al.¹⁴ and Ibrahim et al.¹⁵ have studied the surface properties and crystal structure of RH ash silica. Crystallization was observed in the samples fired at and above 800°C. Krishnarao et al.¹⁶ reported the change in morphology of RH silica [Fig. 6(a)] after crystallisation at 1200°C. The size of RH ash decreased [Fig. 6(b)], and its surface appeared smooth [Fig. 6(c)]. This was attributed to the potassium that causes surface melting and acceleration of the crystallisation of amorphous silica.

Concha Real et al.¹⁷ reported that preliminary leaching of RHs with a solution of HCl acid before their combustion at 600°C produces a silica ash with very high surface area ($\approx 260 \text{ m}^2/\text{g}$). The specific surface area of untreated RH silica ash decreased to $< 1 \text{ m}^2/\text{g}$. For a similar reason (low surface area) the weight loss due to the removal of moisture and adsorbed gases was low for silica obtained from RRH (Table 1). If the heat treatment at 1000°C for 3 h had removed the retained carbon (fixed carbon), the weight loss for RRH samples should be higher than that for TRH1 and TRH2. In TRH1 and TRH2 the loss was high, due to their high surface area. From the above observations the formation of black carbon fixed particles can be explained. When RHs are heated from room temperature, the organic matter like cellulose, lignin etc. decomposes into carbon. Further rise in temperature causes oxidation of carbon. Before the removal of all the carbon, if the temperature is raised to the decomposition temperature of K_2O where surface melting of the ash occur, the carbon will get entrapped in the melt. If RHs are slowly heated, the

Table 1
Impurity analysis in wt.% of rice husk ash (silica) obtained at 700°C

Impurities	RRH slow heating	TRH1 slow heating	TRH2 slow heating	RRH sudden heating	Melting point of impurity K
Wt. loss at 1000°C/3 h	2.390	7.6000	6.8000	2.2900	–
SiO ₂	90.2000	92.2000	92.3000	89.8000	1880
Al ₂ O ₃	0.2682	0.0680	0.0604	0.2908	2290
MgO	0.0270	0.0060	0.0023	0.0332	3100
CaO	0.0690	0.0014	0.0010	0.0630	2850
MnO ₂	0.1070	0.0010	0.0030	0.1170	808 dissociates
Fe ₂ O ₃	0.0290	0.0110	0.0830	0.0400	1838
Na ₂ O	0.1010	0.0124	0.0150	0.0890	1548 sublimes
K ₂ O	2.1200	0.0180	0.0130	2.5800	620 dissociates
P ₂ O ₅	0.4700	0.0110	0.0050	0.4300	850
Carbon residue	4.2188	0.0712	0.7173	4.2770	–

carbon could oxidise before it reaches the dissociation temperature of K_2O . During sudden heating of RRH, the RHs samples were suddenly introduced into the furnace maintained at higher temperature. This causes simultaneous oxidation of carbon formed from decomposition of organic matter and dissociation of K_2O followed by surface melting. Once carbon is entrapped in the potassium rich melt, it can not be oxidised as it is not in direct contact with air. As the temperature of calcination increases, the tendency of carbon fixation increases during sudden heating. Therefore, a large number of black particles were observed in the suddenly heated RRH at 600 and 700°C.

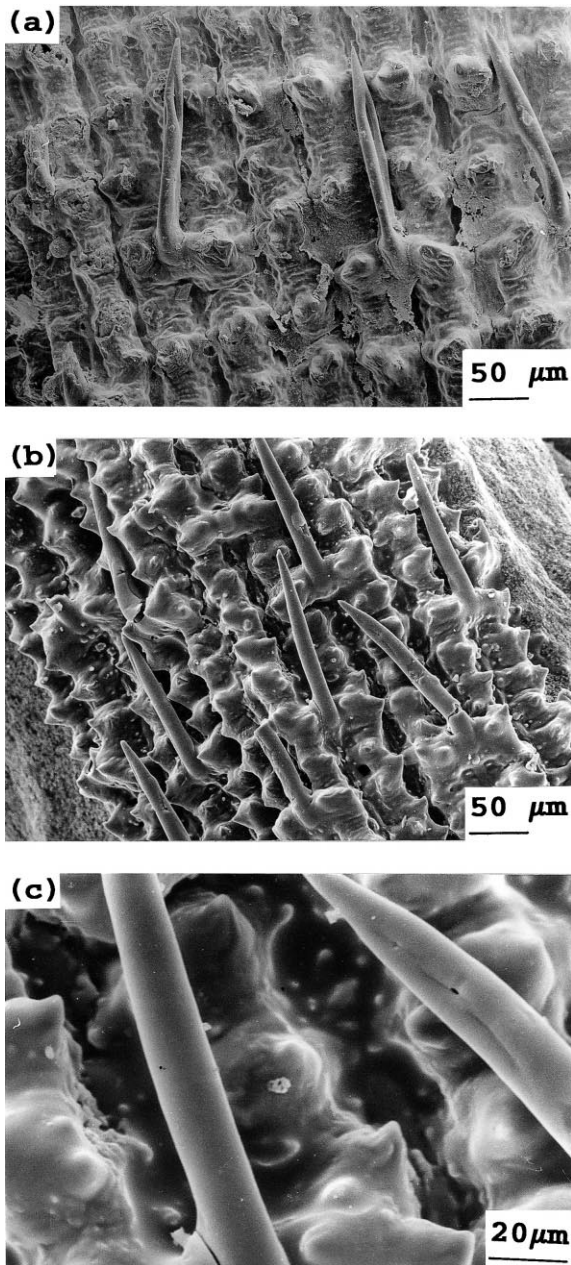


Fig. 6. SEM micrographs of (a) RRH silica obtained by calcining at 700°C, (b) and (c) after heat-treating for 1 h at 1200°C.

During slow heating the carbon formation and its oxidation occurs before the dissociation of K_2O and surface melting. So the tendency of silica for retention of carbon is eliminated. But the silica formed from untreated RHs is not so bright (white) as silica formed from treated RHs. This is due to the removal of impurities including potassium by acid treatment. Due to the absence of potassium there is no effect of rapid (sudden) heating on the formation of black particles in acid treated RHs. To study the effect of potassium, the TRH1 sample was impregnated with 4 wt.% of K_2CO_3 . The potassium carbonate powder was dissolved in de-ionised water and added to the TRH1. After soaking for 1 h, they were dried in an oven at 90°C for 15 h. The K_2CO_3 treated TRH1 was calcined at 700°C for 3 h by slow heating and by sudden heating. The appearance of

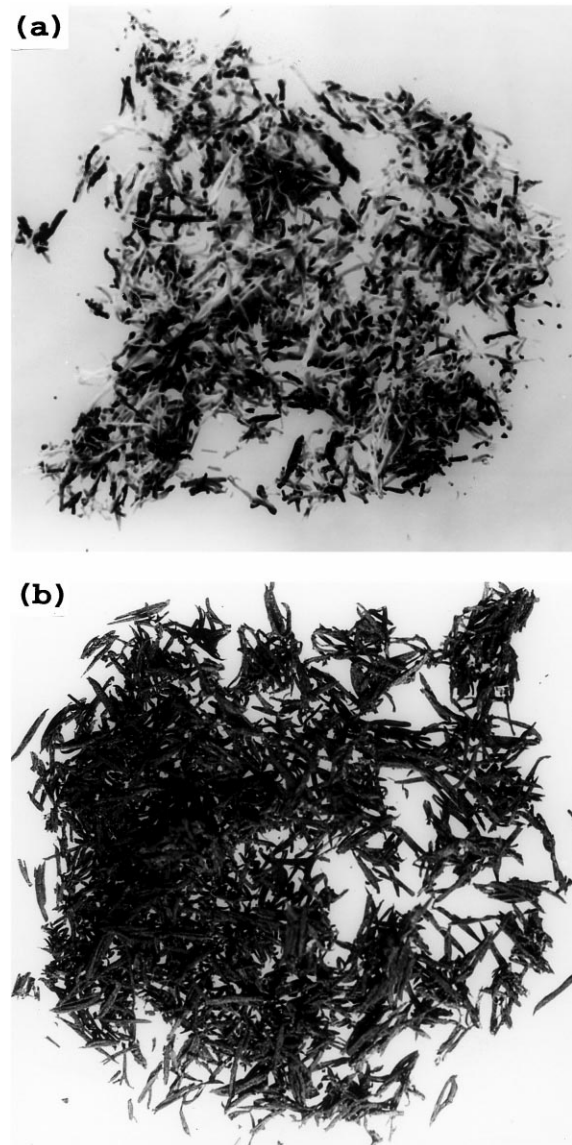


Fig. 7. The appearance of K_2CO_3 treated TRH1 after calcining at 700°C for 3 h (a) by slow heating and (b) by sudden heating.

silica ashes was similar to that of RRH samples. In the slowly heated sample a number of black particles appeared [Fig. 7(a)]. The sample subjected to sudden heating has an appearance of charred RHs [Fig. 7(b)]. The ash particles were sticking to each other and to the sample holder (stainless steel tray). This is a clear evidence of fusion of potassium and its effect on burning of carbon formed from organic matter in RH.

However, at low temperatures (400 and 500°C) the oxidation of carbon in the acid treated RHs is sluggish. To confirm this result, the TRH1 and TRH2 samples were calcined at 400 and 500°C in another muffle furnace. Ash of reasonable whiteness was formed after heating for 16 h at 400°C. Thus the present investigation revealed, that potassium is the main impurity element causing the formation of black carbon fixed particles in the silica ash from RHs. The time taken for acid treatment of RHs can be compensated by resorting to rapid heating or burning to produce pure amorphous bright white silica.

5. Conclusions

Effect of three parameters (acid treatment, temperature and heating rate) on the formation of black (carbon fixed) particles in rice husk silica ash was studied. The black particles in the rice husk silica are due to the carbon fixed in them. This happens due to surface melting of silica in the presence of K_2O impurity. In the acid treated samples, the impurity removed and hence no carbon appears in the silica ash. In untreated samples, rapid heating does not allow the oxidation of carbon before the surface melting occurs, resulting in a higher amount of black particles. On the other hand, slow heating allows oxidation of carbon before surface melting of silica, resulting in a silica ash with negligible black particles. However, at low temperature (400°C) the oxidation of carbon in the acid treated rice husk is sluggish.

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