Effect of calcination temperature and heating rate on the optical properties and reactivity of rice husk ash

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Abstract Rice husk is an agricultural waste and its conversion to value added products makes it a secondary resource material. On heating, rice husk gives ash with >90% by weight of silica with some carbon and other nonmetallic and metallic impurities. Silica of high purity, chemical reactivity and white color can be produced from rice husk by controlling the heating conditions and this material finds wide industrial applications. Properties of the ash depend upon various pretreatments and calcination conditions. The present work deals with the investigation on a rice husk sample from the state of Andhra Pradesh in India. The raw husk and its acid treated form were calcined at different conditions such as temperatures, soaking periods and heating rates. Lime reactivity, surface area, brightness and color values of the ash samples were measured. The high potassium content in the husk has been found to inhibit the carbon removal during ashing which affected the color as well as reactivity of the ash. Properties of the ash samples from the untreated and acid treated husk have been compared and correlated with the formation conditions.

Introduction

Rice husk is an abundantly available waste material in all rice producing countries. It is reported that for every ton of rice produced, nearly 0.23 tons of husk is formed. The production of rice husk in India is nearly 26 million tons [1] and hence its efficient utilization is urgently needed to avoid environmental pollution. In certain regions, the husk is used as a fuel for parboiling paddy in the rice mills. The partially burnt rice husk thus produced also contributes to pollution. Recently, efforts are being made not only to overcome the pollution but also to find value addition to these wastes by using them as secondary resource materials. Formation of reactive silica from rice husk is a simple process compared to other conventional techniques for its production. Thus, any process to produce this silica from rice husk has the benefit of not only getting valuable material but also of reducing disposal and pollution problems of the husk.

Rice husk on burning gives 14–20% by weight ash which contains ~90% by weight silica and minor amounts of other elements. Under controlled burning conditions amorphous silica with high reactivity, ultra fine size and large surface area can be produced [2–4]. The quality of ash prepared depends on various heating conditions like temperature, rate of heating, and soaking time. A review article on the processing, properties and applications of reactive silica from rice husk has been recently published from our laboratory [5]. The ash is used as a good pozzolana in cement industry [6–8] and also as a support material for metal catalysts. Preparation of different value added products like silicon carbide, porous carbon, zeolites, cordierite, etc from rice husk ash has been reported [9–17]. The ash finds extensive uses as filler, additive, abrasive, oil adsorbent, sweeping component, suspension agent for porcelain enamels etc [18–22]. Each application requires specific properties such as reactivity for cement and concrete, chemical purity for synthesizing advanced materials,

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whiteness and proper particle size for filler applications and high surface area and porosity for use as adsorbent and catalyst.

The ash obtained from rice husk under controlled heating conditions is widely used in lime-pozzolana mixes. Pozzolans are siliceous and aluminous materials, which in finely divided form and in presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties [23]. Pozzolanic materials are added to cement to fix the free lime by clinker silicates during their hydration. This causes free lime to become insoluble in water, making the cement highly resistant to environmental effects. When a part of cement is replaced with pozzolanic material, the plasticity of concrete increases and the hydration heat of cement are reduced [24]. At temperatures around 30 °C and in presence of water, the amorphous silica in rice husk ash can react with $Ca(OH)_2$ to form a kind of C–S–H gel ($Ca_{1.5} SiO_{3.5} xH_2O$). The C–S–H gel looks like flocs in morphology with a porous structure and large specific surface. When this product is heated, it loses the water, but maintains an amorphous form up to 750 °C. Above 780 °C it begins to transform to crystalline $CaSiO_3$. One of the main reasons for the improvement of concrete properties upon addition of rice husk ash possibly may be attributed to the formation of more C–S–H gel in concrete due to the reaction occurring between silica in the ash and the Ca^{2+}, OH^- ions or $Ca(OH)_2$ in hydrating cement [25, 26]. The amorphous silica with high surface area produced from rice husk can be used as a pozzolan. The ultrafine size makes it excellent filler which goes into the micro voids giving high strength to the concrete [27].

White color is preferred for silica in most of the filler applications. Measurement of optical properties is essential to quantify the color of the material. Brightness, whiteness, yellowness and **Lab** color values (expressed in ISO units) constitute the important optical properties which are stringent for white pigments. Brightness represents the % of reflectance of light at a wavelength of 457 nm and the difference in reflectance values at 457 and 570 nm gives the yellowness. Hunter whiteness and yellowness indices have the advantage of single number quantities that are based on the entire visible spectrum. The whiteness formula relates better to people's visual assessment than brightness whereas yellowness indices normally do not correlate well with the visual judgment of yellowness. The **Lab** system based on the color opposites gives a better representation of the colors. The term **L** is a measure of lightness/darkness and varies from 100 for perfect white to 0 for absolute black. The red/green color is indicated by **a**. The more positive is its value, greater is the reddishness

and negative value indicating greenishness. Similarly, the yellow/blue shade is represented by **b**, positive value for yellow and negative for blue.

The rice husk ash is slightly blackish due to the presence of unburned carbon. Hence, the brightness/whiteness is generally low and L is more significant among the color values. The formation of black particles during the combustion of rice husk is studied by Krishna Rao et al. and carbon appears to get fixed in the ash matrix due to surface melting of silica in presence of low melting alkalies especially potassium [28]. Rapid heating of the rice husk does not allow the oxidation of carbon before the surface melting occurs, resulting in a higher amount of black particles. But if the heating rate is lowered, oxidation of carbon takes place before surface melting of silica and the amount of black particles is considerably reduced. Treatment of the husk with dilute acids also reduces the carbon and other impurities. Sidheswaran et al. prepared pure white amorphous silica by pretreating the husk by HNO_3 followed by ashing and measured the whiteness using a color scanner [29]. Real et al. have studied the preparation and properties of high purity silica with high surface area from rice husk containing ~5.5% K_2O [30]. Recently, effect of pre-treatments with various mineral and organic acids on the optical properties of two rice husk samples of different origin has been reported from our laboratory [31]. However, the effect of heating conditions on the optical properties of ash has not been studied so far. All the reported data gives only the visual evaluation of the color, in a qualitative manner. The present work involves the studies on the effect of different calcination conditions on the optical properties and lime reactivity of a rice husk sample with ~2.5% K_2O collected from the central part of India.

Experimental

Raw material

Rice husk from Vijayawada (~79° North of equator and 15° East of Greenwich), Andhra Pradesh State of India is selected for the investigation. The sample was washed thoroughly with water to remove the soluble particles and dust whereby the heavy impurities like sand are also removed. It was then dried in an air oven at ~110 °C for nearly 6–8 h.

Acid treatment

About 500 mL 0.1 N HCl was added to 50 g rice husk and boiled for 1 h with frequent stirring. The acid was

decanted and the sample was washed thoroughly with distilled water till free from acid and dried at about 110 °C.

Thermal treatment

The rice husk as well as the acid treated husk was subjected to heat treatment to get the ash. About 12 g of the husk was taken in silica crucible and heated at different temperatures from 500 °C to 1000 °C at an interval of 100 °C in a programmable furnace. The heating rate was maintained at 5 °C/min. Samples were withdrawn at different soaking time. For each temperature the soaking times were 2, 4 and 6. The ash samples are designated with temperatures and soaking time figures i.e. Tt, T represents the temperature of calcination and t represents soaking time in hours. For example the ash sample prepared at 500 °C with a soaking time of 2 h is designated as RHA 5002 with $T = 500$ and $t = 2$.

To study the effect of rate of heating on the properties of the ash, a temperature of 700 °C and soaking time 2 h were selected which are the conditions optimized in our laboratory for the preparation of amorphous and reactive silica from rice husk [4]. Ash samples were prepared at different heating rates like 1, 2, 3, 5, 7 and 10 °C/min and characterized.

Characterization

X-ray diffraction patterns of the ash samples were taken using a Philips X—ray diffractometer (model PW1710) with CuKα radiation and Ni filter. The powder sample for the XRD was prepared by putting a thin layer of powder smeared over a glass plate. The glass plate was previously coated with paraffin wax to get good adhesion. The XRD analysis was carried out at a voltage of 40 kV and 30 mA current intensity. The 2q step was 0.06 and the step time was 40 s/step.

The ash samples prepared at different conditions were examined for their color by measuring the optical properties such as brightness, color values and whiteness using a Colour Touch^{TM} model ISO Spectrophotometer (Technidyne Corporation, USA). The sample was dried in an air oven at 110 °C for one hour, cooled and pulverized for 10 s using an Anglo Pulveriser. It was then made into a pellet by applying a pressure of 561 kPa for 30 s in a Powder Press Apparatus. Then the pelletized sample was introduced into the instrument and the measurements were taken.

Standard wet chemical methods supported with instrumental techniques were adopted to determine the chemical constituents. SiO_2 was estimated gravimetrically by hydrofluoric acid evaporation, iron and manganese by colorimetric method (Jenway 6405) and the alkalies using flame photometer (Systronics 128). Loss on ignition (LOI) as found out by heating the sample to 1,000 °C for 1 h.

Reactivity of the ash was determined by chemical method [32]. Known amount of the sample was treated with saturated $Ca(OH)_2$ solution which reacted with the silica. The unused Ca was estimated by complexometric titrations. The drop in Ca ion concentration in the solution corresponds to the calcium, which reacted with the silica in the ash. The lime reactivity was calculated from the difference in Ca concentration before and after treatment with the ash and is expressed as mg CaO/g of the ash. The surface area and pore volume were measured by BET nitrogen adsorption method at –196 °C using Micromeritics Flow Prep 060 model surface area analyzer.

Results and discussion

Black particles were found in all the ash samples irrespective of the temperature and time of ashing. However, pretreatment of the rice husk with dilute hydrochloric acid followed by heat treatment was found to give ash almost white in color. The ash samples from the untreated and acid treated rice husk are designated as RHA and *RHA respectively.

Chemical assay

Ash content of the rice husk before and after acid treatment was found to be 17.6 and 18.4 respectively. Acid treatment removed considerable amounts of metal ion impurities and Table 1 gives the chemical constituents of the ash samples. The silica content of the ash is ~90% by weight which goes up to ~97.7% for the acid treated husk. Subsequently, the Na, K, Ca, Fe and Mn contents come down to a great extent. The LOI corresponds to the volatile organics as well as the

Table 1 Chemical assay of untreated and acid treated rice husk ash

Constituents, % by wt.	RHA	*RHA
SiO_2	89.50	97.81
Na_2O	0.28	0.07
K_2O	2.47	0.39
CaO	1.84	1.05
Fe_2O_3	0.41	0.15
LOI	1.85	2.11
Mn ppm	56.44	3.31

moisture content of the ash. After the removal of the volatiles, the product ash still shows some ignition loss which can be attributed to the loss of adsorbed moisture and surface hydroxyl groups in silica [2]. However, it is interesting to note that in spite of the presence of black carbon particles in the ash, the LOI is almost equal to that of the ash obtained from the acid treated husk. This conclusively proves that the black particles have 'fixed' carbon.

X- ray diffraction studies

The XRD patterns of the selected ash samples, RHA5002, RHA7002 and RHA9002 are represented by Fig. 1. Only peaks corresponding to graphite are observed for RHA 5002 and RHA7002. The RHA 9002 shows a peak at 22.2° 2θ which is reported to be that of disordered cristobalite, a crystalline form of silica. Fig. 2 gives the XRD patterns of the corresponding products from the acid treated husk, *RHA5002, *RHA7002 and *RHA9002. Presence of carbon is indicated in *RHA5002 whereas neither carbon nor crystalline silica is present in *RHA7002. Peaks of cristobalite appear in *RHA9002. As mentioned earlier, the ash contains fixed carbon which does not burn off even at 1,000 °C. The ash also contains significant amount of K_2O which may be dissociating at low temperature to form elemental potassium. This phenomenon causes surface melting and the carbon gets entrapped in this melt. The direct contact with air is lost and its oxidation on further heating is prevented [28]. Thus the high percentage of K_2O in the rice husk sample contributes to the formation of black particles

during the combustion. However, acid treatment of the husk removes most of the potassium and the ash becomes free of fixed carbon. It is reported that porous or activated carbon can be produced by heating rice husk at a relatively lower temperature in presence of "chemical activators" such as KOH, K_2CO_3, and Na_2CO_3. The peak corresponding to cristobalite in the RH9002 is found to be bigger than that of *RH9002. The presence of carbon is accelerating the formation of cristobalite as observed by Wu et al. [33] whereas this phenomenon is occurring due to the presence of potassium according to Krishna Rao et al. [28]. The crystalllization of trydimite silica from rice husk at higher temperature (1300 °C) in presence of potassium ions has been established by Real et al. [30]. The formation of nano-structured silica during carbonization and combustion of rice husk has been discussed by Liou in his recent publication [34].

Surface area

High surface area and pore volume are typical properties of materials which can be used as adsorbents. Activated carbon and silica are well known adsorbents with wide industrial applications. Selected rice husk ash samples were analyzed for these properties and the values are given in Table 2. The reactivity of silica is directly related to its amorphous nature and surface area. The rice husk ash under the present study is found to have very low surface area and pore volume and acid treatment of the husk followed by heating gives ash with considerable improvement in these values [31]. As described by Real et al., a strong
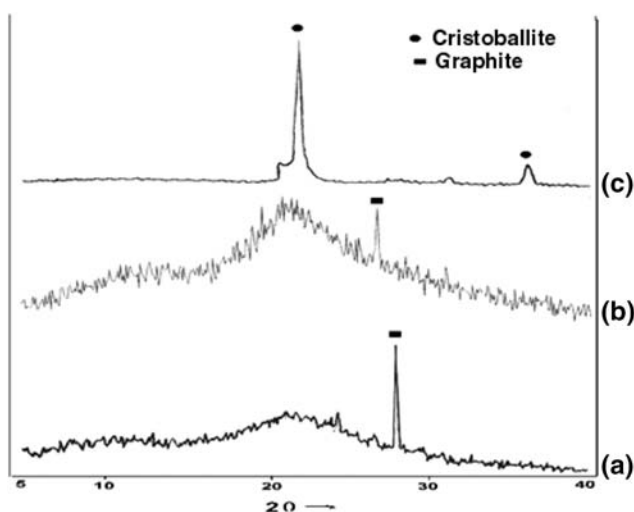

Fig. 1 X-ray diffraction (XRD) patterns of rice husk ash samples. (a) RHA 5002, (b) RHA 7002 and (c) RHA 9002
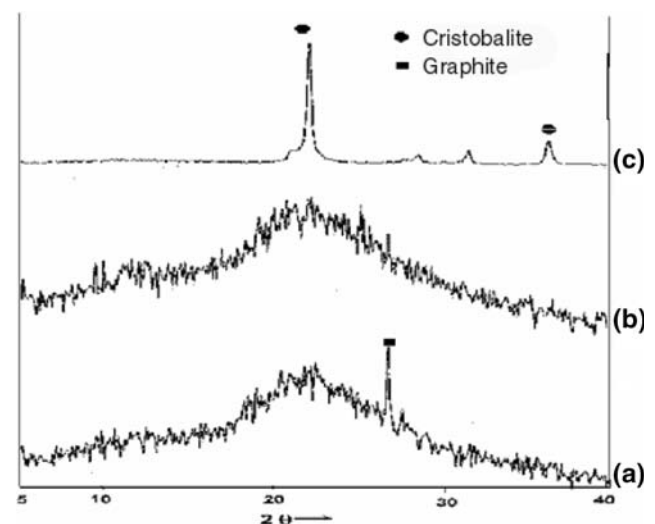

Fig. 2 X-ray diffraction (XRD) patterns of rice husk ash samples. (a) *RHA 5002, (b) *RHA 7002 and (c) *RHA 9002

Table 2 Surface area and pore volume of RHA 7002 prepared at different heating rates

Rate of heating (°C/min)	Surface area (m²/g)	Pore volume (cm³/g)
1	11.53	0.0071
2	10.44	0.0062
3	7.61	0.0039
5	9.30	0.0054
7	18.99	0.0084
10	50.20	0.0245

interaction occurs between the potassium ions and silica which leads to a dramatic increase in particle size and considerable decrease in surface area [30].
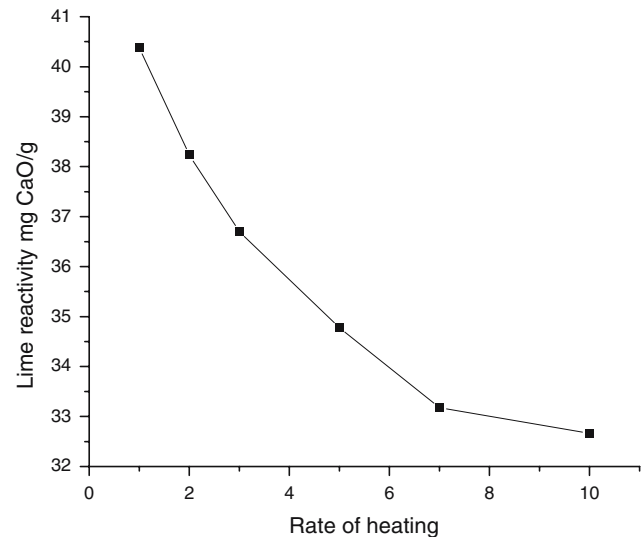
The rate of heating is also found to influence the surface area of the ash. With increasing rate of heating, surface area first decreases from 1 °C/min to 5 °C/min and then increases up to 10 °C/min. The surface area values and pore volume of the ash samples prepared at different rates of heating is given in Table 2. Crystallization of the SiO_2 to cristobalite generally brings down the surface area. The higher surface area for the ash formed at lower heating rate is due to the slow crystallization. At higher heating rate, more carbon is formed which may be attributing to the increase in surface area in spite of the higher crystallization rate.

Lime reactivity

Chemical reactivity of the ash comes down drastically with the formation of crystalline isomers like cristobalite, tridymite and quartz. Hence, the silica has to be totally amorphous to have high reactivity. Table 3 and Fig. 3 give the lime reactivity values of the ash samples prepared at different conditions. The value is found to decrease with increasing temperature, soaking time and decreasing heating rates. At higher rate of combustion, amorphous silica is formed but at lower rates, part of the silica crystallizes. It is reported that crystallization of silica can be prevented by

Fig. 3 Variation of lime reactivity with rate of heating

controlling the temperature, time of burning and rate of heating [4]. Heating of ash to higher temperatures and long soaking time converts the amorphous SiO_2 into crystalline forms.

The amount of free lime combined by pozzolanic material is an indication of its pozzolanic property. This property depends greatly on the surface area of the pozzolana. The rate of increase and decrease of lime reactivity is found to vary with the ashing temperature (Table 3). More reactive silica is forming in the ash as the carbon gets oxidized. As the rate of heating increases, the lime reactivity decreases. However, with a decrease in the rate of heating, the amorphous silica is converted to crystalline form where by the lime reactivity decreases. The variation of lime reactivity with rate of heating is shown in the Fig. 3.

The lime reactivity values of the untreated and acid treated products are given in the Table 3. During acid treatment potassium ions are leached out and the weight % of SiO_2 in the acid treated rice husk ash is

Table 3 Lime reactivity values of rice husk ash samples prepared at various conditions

Samples	Lime reactivity (mg CaO/g)	Samples	Lime reactivity (mg CaO/g)	Samples (different rate of heating)	Lime reactivity (mg CaO /g)
RHA 5002	61.49	*RHA 5002	120.52	RHA 7002 (1)	40.38
RHA 5004	74.79	*RHA 5004	124.98	RHA 7002 (2)	38.23
RHA 5006	74.28	*RHA 5006	141.19	RHA 7002 (3)	36.70
RHA 6002	33.52	*RHA 6002	119.76	RHA 7002 (5)	15.15
RHA 6004	17.29	*RHA 6004	120.10	RHA 7002 (7)	33.18
RHA 6006	18.55	*RHA 6006	120.12	RHA 7002 (10)	32.66
RHA 7002	15.15	*RHA 7002	109.04	–	–
RHA 7004	19.28	*RHA 7004	129.36	–	–
RHA 7006	11.00	*RHA 7006	129.29	–	–
RHA 9002	16.21	–	–	–	–
RHA 10002	13.59	–	–	–	–

higher than that in the untreated product. Thus the carbon content is much less and there is no surface melting and silica crystallization. This may be the reason for the higher lime reactivity of these samples.

Optical properties

Cellulose forms the main body of raw husk and when the latter is subjected to acid treatment, cellulose is reduced, i.e., the carbohydrates are blackened due to the removal of oxygen. The proteins in the husk are decomposed into amino acids, and the cellulose of larger molecular weight is leached out as smaller molecular weight compounds. From the chemical analysis, it is clear that the impurities in rice husk are substantially removed by acid treatment.

The optical properties are dependent on the color imparted by the carbon produced on heating the ash which partly gets burnt off at higher temperature/soaking time. The colored oxides of metallic impurities also play an important role, but become insignificant in presence of the black carbon which masks other colors. Hence L value is more relevant. For untreated husk, the ash RHA 5002 is having lowest brightness, L, and H_W values (Table 4a). Increasing soaking time improves these values. The RHA 6002 is having higher

values compared to RHA 5002 which again increase with the soaking time. Similar trend is found in the RHA 700 series also. However, RHA 9002 and RHA 10002 are found to have inferior optical properties. In most of the samples, brightness, L and H_W values follow the same trend. The values for a and b are too small and insignificant whereas the H_Y values did not find any direct relation with the brightness. This can be attributed to the masking of yellow shade by the more prominent black color.

For acid treated products, the oxidation of carbon at low temperature is sluggish. The brightness, L, and H_W increase with increasing temperature and soaking time (Table 4b). The highest values are for *RHA 6004. The maximum a, b and H_Y values are found to be for *RHA 5006. The brightness and H_W values of acid treated products *RHA 5002, *RHA 5004 and *RHA 5006 are less than the corresponding untreated products. At higher temperatures, the trend becomes the reverse.

For studying the effect of rate of heating on the optical properties, the temperature as 700 °C and soaking time as 2 h were selected. It is found that as the rate of heating is increased, the optical properties like brightness, L, a, b, H_W and H_Y deteriorates. The brightness values are 39.96 and 10.51 when the rates of

Table 4 (a) Optical properties of ash samples from untreated husk (RHA), (b) optical properties of ash samples from 0.1 HCl acid treated rice husk (*RHA) and (c) optical properties of RHA 7002 at different rate of heating

| Samples	Brightness % ISO	L, a, b	H_W	H_Y
(a) Optical properties of ash samples from untreated husk (RHA)				
RHA 5002	9.85	31.54, 0.35, 0.24	9.52	1.08
RHA 5004	44.54	69.13, 0.92, 0.36	34.50	6.95
RHA 5006	35.39	60.87, 0.48, 1.96	30.23	4.61
RHA 6002	28.03	53.90, 0.24, 1.31	25.01	3.48
RHA 6004	26.76	51.24, 0.46, –0.78	28.53	–2.16
RHA 6006	28.70	53.26, 0.46, –0.49	29.86	–1.32
RHA 7002	20.21	43.91, 0.29, –1.52	23.10	–4.95
RHA 7004	23.28	46.99, 0.31, –1.83	27.00	–5.57
RHA 7006	26.04	49.60, 0.41, –2.13	30.65	–6.14
RHA 9002	16.36	40.67, 0.37, 0.33	15.78	1.14
RHA 10002	20.52	45.54, 0.28, 0.33	19.88	1.04
*(b) Optical properties of ash samples from 0.1 HCl acid treated rice husk (*RHA)*				
*RHA 5002	2.67	17.08, 0.78, 1.31	1.63	10.99
*RHA 5004	7.09	28.81, 1.48, 2.98	3.39	14.79
*RHA 5006	17.14	45.52, 2.06, 5.61	6.13	17.60
*RHA 6002	21.60	47.12, 0.42, 0.92	19.73	2.78
*RHA 6004	61.61	79.67, 0.29, 1.69	55.78	3.03
*RHA 6006	50.56	72.22, 0.98, 1.58	45.65	3.12
*RHA 7002	53.25	73.42, 0.11, 0.66	51.14	1.28
*RHA 7004	55.66	75.19, 0.28, 0.84	52.94	1.59
*RHA 7006	57.98	77.04, 0.35, 1.28	53.72	2.37
(c) Optical properties of RHA 7002 at different rate of heating				
1	39.96	62.85, 0.72, –0.75	41.45	-1.24
2	37.84	61.10, 0.58, –0.63	39.52	-1.47
3	29.05	52.98, 0.50, –1.37	32.20	-3.68
5	20.21	43.91, 0.29, –1.52	23.10	-4.95
7	13.68	35.9, 0.28, –1.58	16.14	-6.30
10	10.51	31.31, 0.19, –1.59	12.64	-7.24
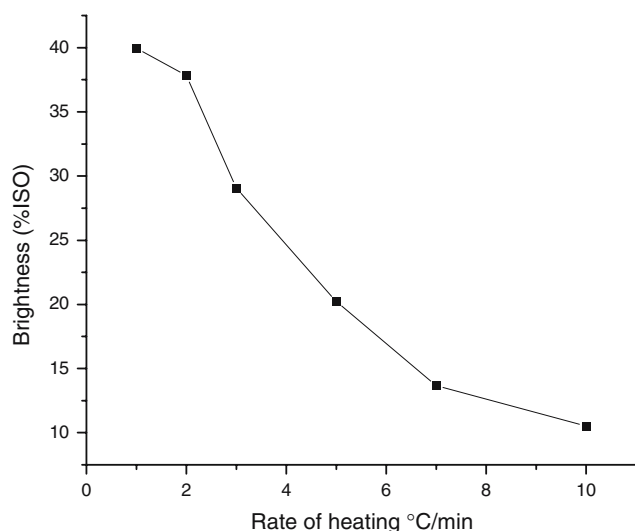
Fig. 4 Variation of brightness with rate of heating

heating are 1 and 10 °C/min respectively. The effect of rate of heating on the brightness of RHA 7002 is shown on the Fig. 3 and the values are given in Table 4c.

The major impurity of the rice husk under study is potassium. The potassium must be accelerating the carbon fixation in rice husk ash. When the husk is heated from room temperature, the organic matters decompose into carbon. Further rise in temperature causes oxidation of carbon. Before the removal of all the carbon, if the temperature was raised to the melting temperature of K_2O, surface melting of the ash occurs and the carbon gets entrapped in the melt. If the husk is slowly heated, part of the carbon gets oxidized before the melting temperature of K_2O is reached resulting in an ash with less black particles [28, 35, 36]. But during rapid heating, the oxidation of carbon and the dissociation of K_2O take place simultaneously. The unburned carbon in the black particles does not get oxidized and removed as it is fixed in the fused silica on the surface and is not in contact with air. When the rice husk is subjected to acid treatment, most of the potassium is removed and the surface melting at low temperature does not occur. Hence, carbon particles are oxidized and burnt off as the temperature and soaking time is increased. The acid treatment, temperature and heating rate have significant effect on the formation of black particles in RH silica ash. (Fig. 4)

Conclusions

Acid treatment and rate of heating of rice husk influence the surface area, lime reactivity and brightness of the ash. Brightness and lime reactivity are enhanced by

acid treatment of the husk and by decreasing the heating rate. The enhancement in brightness achieved by the former treatment is found to be higher than that by the latter one. As the heating rate increases, surface area decreases initially and then increases. Rapid heating of the rice husk produces more black particles which contain fixed carbon. The potassium in the rice husk causes surface melting at low temperature and the carbon gets entrapped giving black color to the ash.

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