

PYROLYTIC PREPARATION OF AMORPHOUS SILICA FROM RICE HUSK

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Preparation of maximum amorphous silica from local rice husk was attempted under controlled heat treatment. A number of batches were pyroprocessed in an electric furnace at 450° - 600°, for 2 - 12 hrs. The resulting ash specimens were analysed chemically and those found with higher silica content studied through XRD. Minor conversion of amorphous rice husk silica to α -quartz phase was observed as a result of heat treatment. The thermal treatment of rice husk at 500° for 8 hrs., yielded the highest percentage of amorphous RHA silica.

Key words: Rice husk, Thermal treatment, Amorphous silica.

Introduction

It has been reported on global basis that about 50% of rice husk (RH) is not properly utilized and about one third is discarded without any use [1]. Similarly millions tons of this important agricultural by-product is wastefully burnt annually in Pakistan [2]. Rice husk ash (RHA) silica, being originally amorphous in nature, is expected to be much reactive as compared with the common crystalline form quartz and therefore can be used in a variety of products.

Although chemical reactivity and amorphous nature of RHA silica are co-related but no hard and fast criteria, concerning the proportions of amorphous or crystalline forms in it i.e. crystalline phase tolerance limits, for its use in different products have been specified. However, it has generally been reported that greater the degree of amorphous character, higher will be reactivity index of the used silica [3].

The silica content of RHA and its mineralogical nature is related to 2 major RH pyroprocessing parameters i.e. time of combustion and temperature. The present study is an attempt to prepare ash, under optimum conditions, containing highest percentage of silica possessing maximum amorphous character. Therefore, investigations to determine its silica content and amorphous or crystalline nature were carried out by chemical analysis and XRD technique. The prepared RH silica, besides its general application, was particularly required for the experimental synthesis of woolastonite (Ca-SiO_2) after its purification through physico-chemical methods.

Experimental

The utilized RH was collected from Gujranwala district, Punjab, Pakistan and belonged to the same crop and place in this area. The procured bulk of RH was thoroughly mixed and

sub-divided to obtain representative samples for experimental work.

Four thoroughly washed and dried RH batches were heat treated in an electric furnace at 500° for 1 - 4 hrs. Heating durations and ash contents have been recorded in Table 1.

TABLE 1. RICE HUSK ASH CONTENTS OF FOUR RH BATCHES HEAT TREATED AT 500° FOR DIFFERENT DURATIONS.

No.	Batch	Ash content (wt.%)	Time (hrs)
1.	RHA-1	21.00	1
2.	RHA-2	20.85	2
3.	RHA-3	20.69	3
4.	RHA-4	20.60	4

Two dozen more RH batches, divided in six groups, were pyro-processed for specified periods of time at different temperatures listed in Table-2. All RHA specimens were completely analysed following the standard procedures of chemical analysis [4-5]. Specimens containing higher content of silica at comparatively lower temperature, were selected for XRD analysis [6-8]. An automated Rigaku powder X-ray diffractometer (Model, D-Max/11-A) was used for this purpose.

Results and Discussion

Average of ash contents came out to be 20.78%, while that reported in literature [9] ranges from 16.30% to 26.00% [2]. The percentage of SiO_2 in all RHA batches was found to vary between 84.48 and 92.01. Complete chemical analysis results of RHA batches listed in Table 2 are given in Table 3.

It is evident from chemical analysis results (Table 3) that batch RHA(E).4(2) i.e. RH thermally treated in electric furnace at 500° for 8 hrs (Table 2), yielded the highest percentage of silica i.e. 92.01%. It has been reported in literature that prolonged treatment of RH at optimum temperature produces

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TABLE 2. RICE HUSK BATCHES PYROPROCESSED UNDER DIFFERENT TIME/TEMPERATURE CONDITIONS.

No.	Batches	Time duration (hrs)					
		2	4	6	8	10	12
		Temperatures (C°)					
1	RHA(E).1(1)*	450	-	-	-	-	-
2	RHA(E).1(2)	500	-	-	-	-	-
3	RHA(E).1(3)	550	-	-	-	-	-
4	RHA(E).1(4)	600	-	-	-	-	-
5	RHA(E).2(1)	-	450	-	-	-	-
6	RHA(E).2(2)	-	500	-	-	-	-
7	RHA(E).2(3)	-	550	-	-	-	-
8	RHA(E).2(4)	-	600	-	-	-	-
9	RHA(E).3(1)	-	-	450	-	-	-
10	RHA(E).3(2)	-	-	500	-	-	-
11	RHA(E).3(3)	-	-	550	-	-	-
12	RHA(E).3(4)	-	-	600	-	-	-
13	RHA(E).4(1)	-	-	-	450	-	-
14	RHA(E).4(2)	-	-	-	500	-	-
15	RHA(E).4(3)	-	-	-	550	-	-
16	RHA(E).4(4)	-	-	-	600	-	-
17	RHA(E).5(1)	-	-	-	-	450	-
18	RHA(E).5(2)	-	-	-	-	500	-
19	RHA(E).5(3)	-	-	-	-	550	-
20	RHA(E).5(4)	-	-	-	-	600	-
21	RHA(E).6(1)	-	-	-	-	-	450
22	RHA(E).6(2)	-	-	-	-	-	500
23	RHA(E).6(3)	-	-	-	-	-	550
24	RHA(E).6(4)	-	-	-	-	-	600

* Rice husk ash prepared in electric furnace.

higher amount of silica [1]. This is due to maximum burning of residual carbon which is evident from lower loss on ignition as reported in Table 3. It has also been observed regarding the nature of such silica that thermal treatment of RH may not only remove the residual carbon but also affects the polymorphic transformation of SiO_2 . Simultaneous occurrence of these phenomena has been observed even at the temperatures up to 1000° [3].

XRD patterns (Figs. 1-3) were found almost similar except for varying intensity of few peaks. All of the XRD patterns clearly show the presence of a broad halo [$2^\circ\theta$] at value of 15-25 which characterises predominant amorphous nature of the materials [3,6,10,11]

The peaks appearing at d(A)- values; 3.343, 2.458, 2.282, 1.817 and 1.540 at Bragg's angles [$2^\circ\theta$]; 26.5, 36.2, 39.4, 50.0, 60.2, respectively are identified as α -quartz crystallites.

The calculated integrated intensities (the area under diffraction curve) of the maximum intensity (I max) for all patterns have been given in Table 4.

The ratio (relative proportions) of integrated intensities came out to be 1.0:1.5:2.0 for the specimens No. 1, 2 and 3 respectively (Table 4). It was noted that RHA batch prepared at 600° for 4 hrs (Fig. 3) and with integrated intensity 379 showed more conversion into α -quartz than the remaining two batches. While, relatively less α -quartz crystallites were developed in the batch prepared at 550° for 4 hrs (Fig. 2), having integrated

TABLE 3. CHEMICAL ANALYSIS RESULTS* (WIGHT PERCENTAGE) OF SIX RHA BATCHES PYROPROCESSED IN ELECTRIC FURNACE.

No.	Batch No.	L.O.I.	SiO_2	A_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
1.	RHA(E).1(1)	9.12	84.48	1.51	0.49	1.63	0.41	0.77	1.61
2.	RHA(E).1(2)	6.63	86.87	1.48	0.50	1.59	0.43	0.75	1.63
3.	RHA(E).1(3)	5.82	87.68	1.50	0.51	1.61	0.45	0.71	1.59
4.	RHA(E).1(4)	2.48	90.42	1.59	0.51	1.53	0.49	0.77	1.59
5.	RHA(E).2(1)	6.27	87.23	1.61	0.47	1.55	0.51	0.73	1.65
6.	RHA(E).2(2)	4.17	89.33	1.53	0.50	1.62	0.42	0.75	1.62
7.	RHA(E).2(3)	2.76	90.11	1.52	0.56	1.65	0.42	0.77	1.64
8.	RHA(E).2(4)	2.26	90.77	1.63	0.55	1.62	0.52	0.77	1.59
9.	RHA(E).3(1)	4.51	88.99	1.49	0.56	1.57	0.48	0.75	1.55
10.	RHA(E).3(2)	2.22	91.42	1.45	0.47	1.55	0.52	0.68	1.51
11.	RHA(E).3(3)	2.11	91.45	1.53	0.45	1.57	0.51	0.77	1.54
12.	RHA(E).3(4)	2.12	91.38	1.57	0.49	1.61	0.43	0.75	1.63
13.	RHA(E).4(1)	3.28	90.22	1.58	0.51	1.60	0.41	0.72	1.57
14.	RHA(E).4(2)	2.01	92.01	1.48	0.41	1.52	0.41	0.63	1.53
15.	RHA(E).4(3)	2.02	91.85	1.47	0.40	1.51	0.41	0.57	1.59
16.	RHA(E).4(4)	2.01	91.90	1.45	0.41	1.60	0.40	0.56	1.51
17.	RHA(E).5(1)	2.95	90.91	1.46	0.43	1.55	0.42	0.55	1.57
18.	RHA(E).5(2)	2.02	91.94	1.51	0.42	1.52	0.47	0.60	1.53
19.	RHA(E).5(3)	2.01	91.86	1.47	0.43	1.53	0.45	0.61	1.56
20.	RHA(E).5(4)	2.01	91.92	1.50	0.42	1.59	0.41	0.63	1.50
21.	RHA(E).6(1)	2.64	90.86	1.52	0.48	1.62	0.42	0.72	1.61
22.	RHA(E).6(2)	2.03	91.95	1.50	0.40	1.51	0.43	0.62	1.53
23.	RHA(E).6(3)	2.02	91.95	1.51	0.41	1.55	0.40	0.61	1.54
24.	RHA(E).6(4)	2.01	91.99	1.50	0.40	1.53	0.41	0.60	1.53

* TiO_2 and P_2O_5 found in traces.

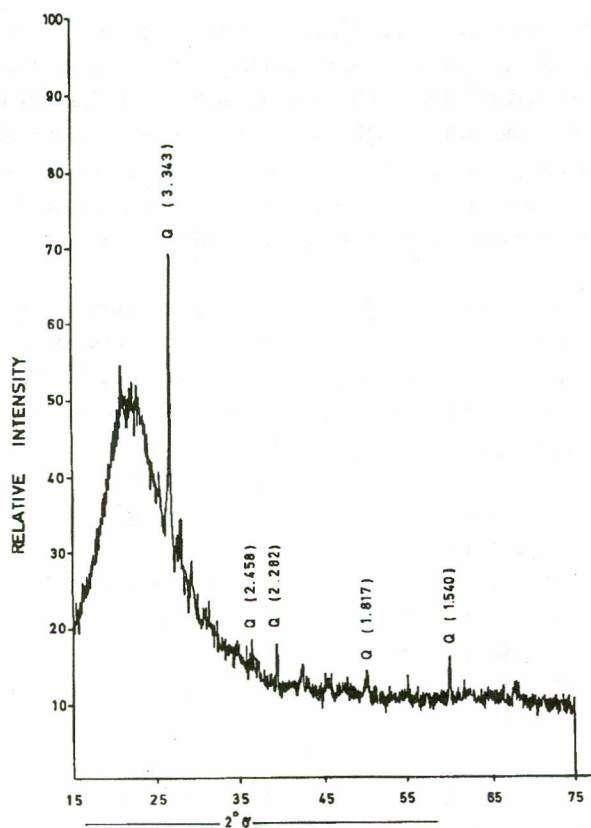


Fig. 1. XRD data ($\text{Cu}_{K\alpha}$) on RHA (E)4. (2), 500°C for 8 hrs.

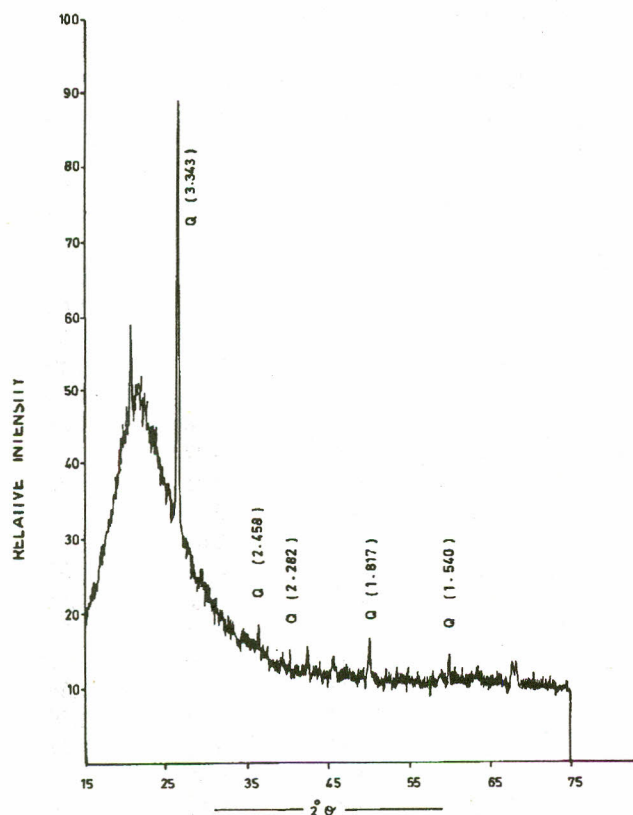


Fig. 2. XRD data ($\text{Cu}_{K\alpha}$) on RHA (E). 2(3), 550°C for 4 hrs.

TABLE 4. INTEGRATED INTENSITIES OF XRD PEAKS WITH MAXIMUM INTENSITIES.

No.	Fig. No. (Pattern)	RHA Batches	Integrated intensity
1.	1	500° C, 8 hrs.	182
2.	2	550° C, 4 hrs.	274
3.	3	600° C, 4 hrs.	379

intensity 274. Similarly, the RH specimen heat treated at 500° for 8 hrs showed minimum α -quartz phase (Integrated intensity, 182).

Chemical analysis (Table 3) and XRD results, when considered collectively, showed that RHA obtained through pyrolytic treatment of RH at 500° for 8 hrs i.e. batch RHA (E). 4(2), consisted of the highest amount of silica (showing least crystalline phase). While, batch prepared at 600° for 4 hrs i.e. RHA (E).2(4), though mainly consisting of silica was found with higher crystalline phase.

Conclusion

Generally, the moderately low temperature processing of RH for longer period seems to be important to obtain higher percentage of silica.

Pyroprocessing of RH at 500° for 8 hrs yielded maximum silica which retained its original amorphous nature upto greater extent. This, on upgradation/purification or in as prepared form may be used according to the requirements.

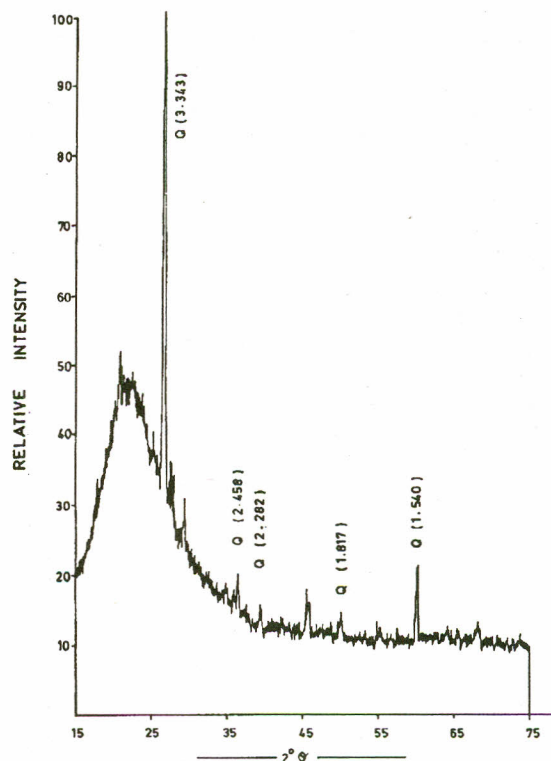


Fig. 3. XRD data ($\text{Cu}_{K\alpha}$) on RHA (E). 2(4), 600°C for 4 hrs.

Although crystalline α -quartz) phase is more or less present in all specimens but at minor level. However, its proportion tend to increase with rise in pyroprocessing temperature.

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Pyrazinone acid hydrazide (1) was prepared [2] by the action of hydrazine on methyl pyrazinone. In this investigation, we report the synthesis of this compound from the reaction between pyrazinoyl chloride and anhydrous hydrazine (1 : 1 mole). However, when the molar ratio of the acid

pyrazinone acid hydrazide A To a solution of pyrazinoyl chloride (1.43g, 10 m. mole) in methylene chloride (20 ml), anhydrous hydrazine (0.32 g; 10 m. mole) was added. The reaction mixture was refluxed for 2 hrs. On cooling yellow crystals separated out, filtered off and recrystallized from ethanol, m.p. 168-69°, yield 87%. This product was shown by direct comparison (m.p. and m.m.p.) to be identical with that reported by Sporn et al. [3].



X = CH₃, R = H
 X = H, R = CH₃
 X = H, R = C₂H₅

TABLE I. PHYSICAL AND SPECTRAL DATA OF THE COMPOUNDS 2a-f.

Comp.	*M.p. (°C)	Yield %	¹ H NMR, δ ppm	IR cm ⁻¹	EIMS
2a	214-15*	81	8.7 (m, 6H), 9.2 (2H) in CH ₂ OH, 9.26 (2H)	1680, 1682	(M ⁺ + 1, 227), 217, 218
2b	218-19**	75	8.71-8.82 (m, 3H), 7.43-7.83 (m, 2H)	1641, 1642	(M ⁺ + 1, 232)
2c	228-29**	82	10.21 (s, 1H), 8.70-9.0 (m, 2H), 6.68-7.93 (m, 3H)	1679, 1679	(M ⁺ + 1, 249), 131, 79
2d	243-44**	80	10.63 (1H), 8.79-9.0 (m, 2H), 7.52-7.80 (m, 3H)	1692, 1692	(M ⁺ + 1, 261), 141, 180, 107, 79, 27, 43
2e	197-98**	83	8.68-8.80 (m, 3H), 2.06 (s, 3H)	1632, 1632	166, 28
2f	153-54**	22.2	8.4 (1H), 7.9 (m, 3H), 2.3 (s, 3H)	1630, 1630	

* Solvent of crystallization: Benzene/ethanol; ** Solvent of crystallization: Ethanol.