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Studies on Thermal Degradation Behavior of Siliceous Agriculture Waste (Rice Husk, Wheat Husk and Bagasse)

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Various siliceous agriculture waste (SAW) such as rice husk, wheat husk and bagasse have been investigated to study their thermal degradation behavior using Thermogravimetric Analyzer (TGA) technique. The focus of this research is to conduct TGA of raw and acid treated (20% HCl & 1M H2SO4) SAW at heating rate 10°C/min in the atmosphere of nitrogen. The results were analyzed on the basis of thermograms and it was inferred that 24 hours soaking with 20% HCl prior to thermal degradation enhanced the percent weight loss. The process also improved the percentage of residual weight of SAW indicating the extraction of amorphous silica with increased purity. The effect of acid treatment was verified by determining chemical composition of SAW samples before and after soaking with 20% HCl. Proximate analysis, thermal degradation temperature ranges and percentage of residual weight at 800°C for each of rice husk, wheat husk and bagasse were also quantified to observe the thermal degradation behavior. XRF analysis was performed to observe the effect of acid treatment for extraction of pure silica.

Keywords: Siliceous agriculture waste, Thermogravimetric Analyzer, amorphous silica.

INTRODUCTION

Biomass is specified as consisting of all plant and plant-derived materials including livestock manures and its structural and chemical compositions are highly variable because of environmental and genetic influences and their interactions[1]. Biomass is also termed as siliceous agriculture waste (SAW) as they provide silica on burning which has numerous industrial applications. In agricultural areas, biomasses are abundantly available and annual production of biomass in Pakistan is approximately 104691 thousand MT/year[2]. Biomass is composed of organic material, 77-80 weight percent (holocellulose, lignin etc.) and inorganic material, 18–20 weight percent (silica, alkali and alkaline earth metals etc.). When acid treated rice husk is burnt under controlled conditions, 550–800°C, highly reactive (amorphous) and pure silica can be obtained[3]. If raw rice husk is burnt under uncurbed conditions then K_2O dissociates due to which black particles (fixed carbon) appears in silica making it impure and converts its amorphous form to crystalline form (less reactive)[4, 5]. If we firstly treat the rice husk with acids and then burn it, the effect of K_2O and other minerals is minimized thus producing amorphous and pure silica[4, 5, 6, 7, 8].

When SAW is thermally treated, it loses weight due to drying and chemical reactions that take place by liberating volatile materials. Thermal gravimetric analysis is an analytical method which determines weight loss of SAW as a function of temperature or heating rate[9]. It is important to comprehend the knowledge about temperature range as high burning temperature (> 1000°C) will render crystalline silica and relatively low burning temperature (550–800°C) will render amorphous silica[6]. Thermal degradation weight loss curves obtained after TGA show three phases; drying (< 100°C), evolution of chemically bond water, devolatilization and degradation of holocellulose (100–400°C) and degradation of lignin (450–650°C)[10].

The current research work is focusing on to conduct TGA of untreated and treated rice husk along with bagasse and wheat straw at heating rate of 10°C/min and to study the effect of acids treatment on the percent weight loss of volatiles, residual weight for each SAW and purity of silica. In the end, XRF analysis was also performed for rice husk.

MATERIAL AND METHOD

Material

The biomasses utilized in the research experimentation were rice husk (RH), wheat husk (WH) and bagasse (B). These biomasses were obtained from Okara District, Punjab. Chemical reagents used in the experiments were 20% HCl, 1M H_2SO_4 and distilled water.

Method

For studying the effect of hydrochloric acid and sulphuric acid on thermal degradation of SAW, fifteen samples were prepared according to the Figure 1. Actions performed on the fifteen samples of RH, WH and B are summarized in Figures 2, 3 and 4 respectively against their identification. Reflex condenser apparatus is utilized for the boiling of rice husk, wheat husk and bagasse

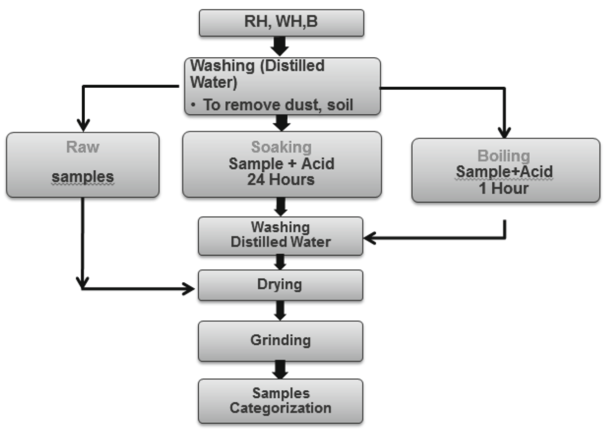

Figure 1. RH, WH and B samples preparation methodology

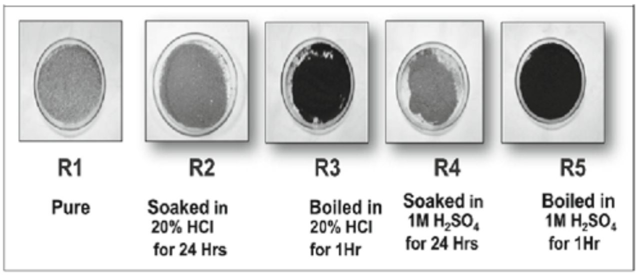

Figure 2. Rice husk samples categorization

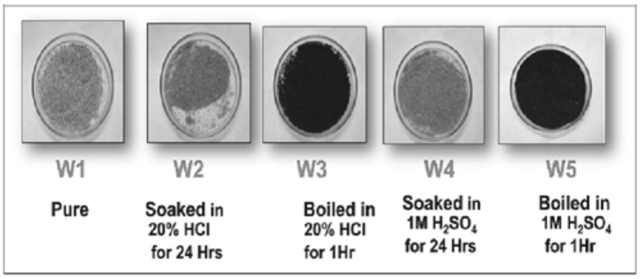

Figure 3. Wheat husk samples categorization

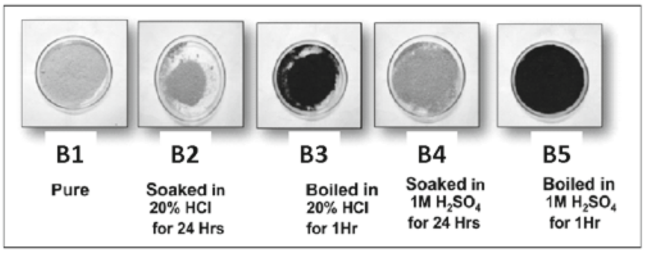

Figure 4. Bagasse samples categorization

samples. Thermal degradation behavior was studied in Thermogravimetric Analyzer (TGA) Q-50 series. XRF analysis was performed to see the effect of acid treatment on the extraction of pure silica from SAW.

Sample R1 was weighed approximately 2~10 mg and was placed into a platinum cup which was housed in the chamber of TGA. The temperature of TGA was maintained at 10°C/min and nitrogen flow rate at 40 ml/min. The nitrogen flow causes the purging of volatiles that liberates during the thermal degradation process of sample under testing. When the heating temperature had risen up to 840°C, the TGA operation was turned off. The TGA signals were sent to computer attached to TGA and all the data was recorded in tabulated form. The recorded data now was used to establish the TGA graphs (thermograms), percentage of residual weight against the temperature in °C. This tabulated data and TGA graph were obtained and used for the data analysis and comparisons.

All the rest of the sample namely R2, R3, R4, R5, W1, W2, W3, W4, W5, B1, B2, B3, B4 and B5 were thermally degraded on the similar pattern as mentioned above for the sample R1.

RESULTS AND DISCUSSION

The results of thermogravimetric analysis have been presented in the form of TGA graphs. The TGA graphs obtained after conducting tests as per the operating conditions mentioned earlier were reproduced below.

TGA Graph for RH, WH and B Samples

It was clearly evident from Figure 5 that thermal degradation of siliceous agriculture waste rice husk occurred in three different stages. In the first stage weight loss occurred due to physically absorbed water. This phenomenon occurred in the temperature range of 40°C to 150°C. Up to temperature range of 150°C, the behavior of all the samples of rice husk whether treated or untreated was almost the same.

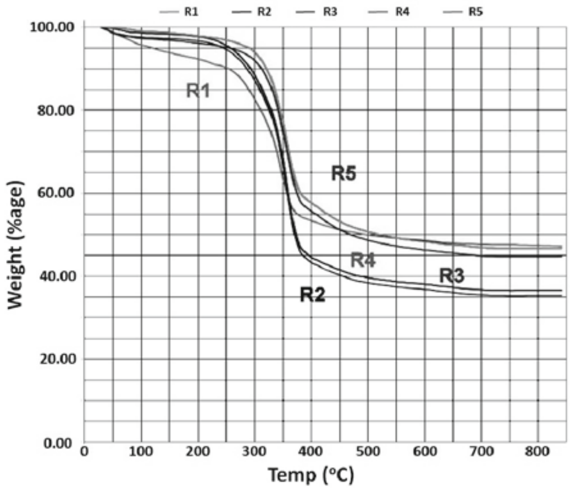

Figure 5. TGA graph for various RH samples

From the Figure 5, it was reflected that in the second stage cellulose and hemicellulose thermally degraded. Thermal degradation of cellulose and hemicellulose resulted in the formation of volatiles such as carbon dioxide, carbon monoxide and char. This phenomenon occurred in the temperature range of 150°C to 400°C. Up to temperature range 400°C, the behavior of rice husk samples started deviating from one another depending upon whether these samples were treated, untreated, soaked or boiled. It was evident from TGA graph that percent weight loss from soaked samples was maximum.

In the final and third stage of thermal degradation, lignin was observed to be thermally degraded. This phenomenon occurred in the temperature range of 400°C to 800°C. It was also evident from TGA graph that thermal degradation of lignin was found to be sluggish. Thermal degradation of lignin typically took place at relatively slow rate and spread over a wide range of temperature from 400°C to 800°C. Further, this stage also indicated that percent weight loss from rice husk soaked sample was on the higher side[10].

Behavior of TGA curves was similar for untreated and treated samples which showed that major contents cellulose, hemicellulose and lignin remained intact irrespective of the acid treatment. The same behavior i.e. three stages was observed with all treated and untreated samples of wheat husk and bagasse. Figure 6 and 7 show the thermograms of wheat husk and bagasse respectively.

Percent Weight Losses of Volatiles for RH, WH and B Samples

Figure 8 has indicated that the percent weight loss was maximum for the rice husk sample R2 at both the temperatures, 400°C and 800°C. It was also concluded that after removal of volatiles, the RH is left with un-

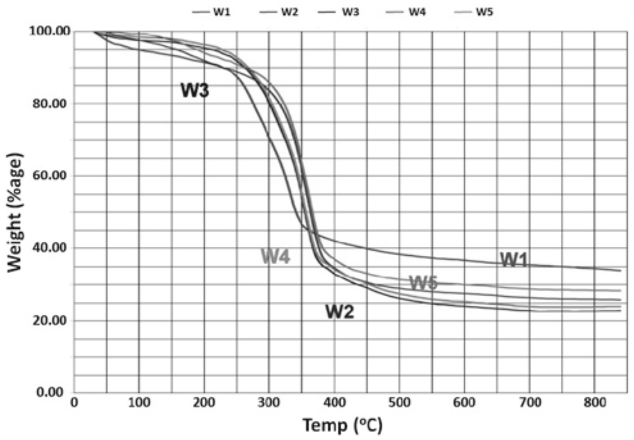

Figure 6. TGA graph for various WH samples

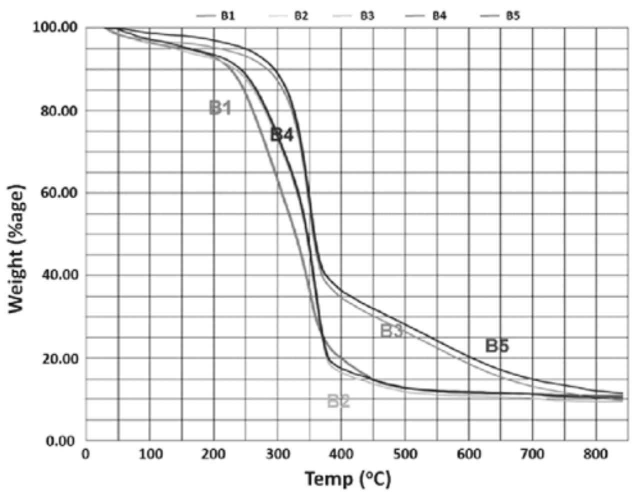

Figure 7. TGA graph for various B samples

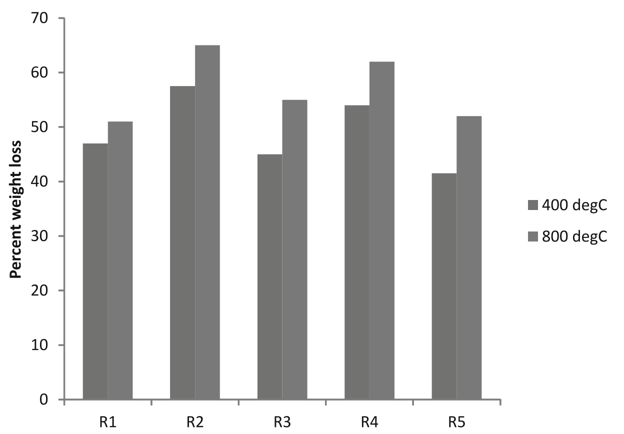

Figure 8. Percent weight loss of RH samples at 400°C and 800°C

-burnt carbon and silica. The reason for choosing 400°C and 800°C for analysis and comparison was that maximum percent weight loss occurred at these temperature points. In case of wheat husk, maximum percent weight loss is shown by sample W2 at both temperatures i.e. 400 and 800°C as shown in Figure 9. While in case of bagasse, Sample B2 shows the maximum weight loss at both temperatures as reflected in Figure 10.

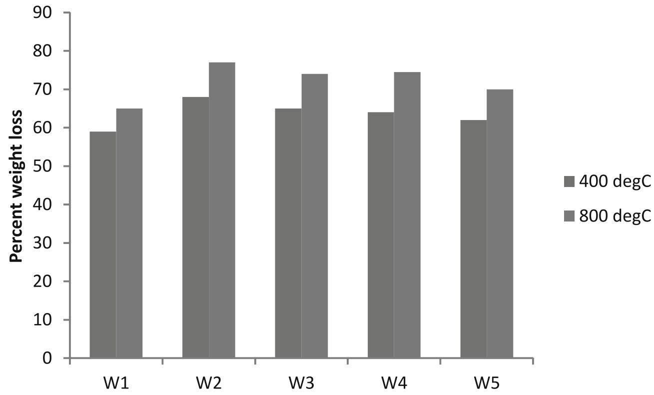

Figure 9. Percent weight loss of WH samples at 400°C and 800°C

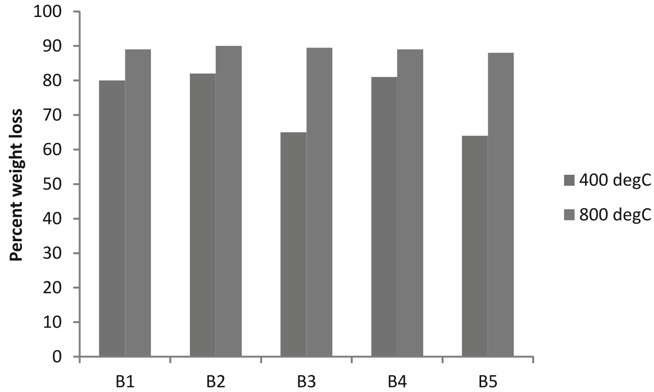

Figure 10. Percent weight loss of B samples at 400°C and 800°C

Percentage of Residual Weight of RH, WH and B samples at 800°C

The reason for comparing the results of residual weights for various samples of rice husk, wheat husk and bagasse at higher temperature level at 800°C was that industrial processes are normally designed above temperature of 700°C for biomass liquefaction and gasification. Figure 11 was evident that rice husk sample, R2, showed the minimum percentage of residual weight on 800°C as compared to other samples of rice husk. This was due the higher percent weight loss of R2 sample during the thermal degradation process. Sample, R2, was soaked in 20% HCl for 24 hours. Wheat husk sample W2 and bagasse sample B2 showed the minimum percentage of residual weight on 800°C as compared to other samples of rice husk. This was due the higher percent weight loss during the thermal degradation process. These samples were soaked in 20% HCl for 24 hours.

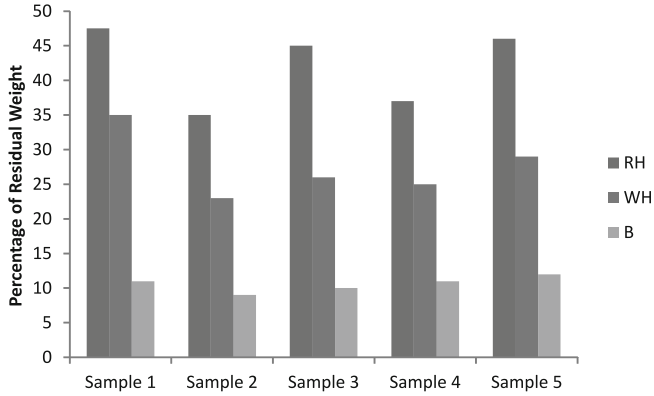

Figure 11. Percentage of residual weight of RH, WH and B samples at 800°C

Proximate Analysis of RH, WH and B Samples from TGA

Proximate analysis which was the determination of moisture content, volatile matter, char content and ash content was also calculated using the Figure 5, 6 and 7, which showed the thermogravimetric analysis graphs for rice husk, wheat husk and bagasse samples. It was evident from Table 1 that volatile matter removal rate was faster in case of rice husk sample R2. This R2 sample was soaked in 20% HCl for 24 hours.

It was evident from Tables 2 and 3 that volatile matter removal rate was faster in case of wheat husk W2. It was soaked in 20% HCl for 24 hours. While in case of bagasse, faster volatile matter removal rate was shown by samples B3 and B5 and they were boiled in 20% HCl and 1M H_2SO_4 for one hour respectively.

Table 1. Proximate analysis of RH samples from TGA

RH Samples	Moisture [%]	Volatile matter [%]	Char and Ash [%]
R1	6.11	46.47	47.42
R2	2.68	62.01	35.31
R3	3.09	52.23	44.68
R4	1.68	61.76	36.56
R5	1.34	51.98	46.68

Table 2. Proximate analysis of WH samples from TGA

WH Samples	Moisture [%]	Volatile matter [%]	Char and Ash [%]
W1	6.54	59.01	34.45
W2	3.03	74.27	22.70
W3	4.65	69.36	25.99
W4	2.11	73.99	23.90
W5	2.47	69.08	28.45

Table 3. Proximate analysis of B samples from TGA

Bagasse Samples	Moisture [%]	Volatile matter [%]	Char and Ash [%]
B1	4.93	84.25	10.82
B2	5.38	85.20	9.42
B3	3.77	85.98	10.25
B4	4.50	85.08	10.42
B5	1.86	85.92	12.22

XRF Analysis of RH sample R2 before and after soaking with 20% HCl and Thermal Degradation

Table 4 shows the XRF analysis of RH sample R2 was conducted before and after soaking with 20% HCl for 24 hours & performing thermal degradation using TGA. Chemical Composition of untreated RH sample contained 89.57% SiO_2 and high concentration 2.58% of impurity K_2O. After treatment soaking with 20% HCl, SiO_2 increased to 97.86% while K_2O reduced to 0.47% which indicates that relatively pure silica was obtained after acid treatment. Same chemical changes are expected when wheat husk and bagasse samples are treated with acid.

Table 4. XRF of RH sample R2 before and after Soaking with 20% HCl for 24 Hrs & Thermal Degradation

Components of RH sample, R2	Composition of R2 before soaking [%]	Composition of R2 after soaking and TGA [%]
SiO_2	89.57	97.86
K_2O	2.58	0.47
TiO_2	0.04	0.02
Al_2O_3	0.38	0.12
Fe_2O_3	0.43	0.03
MnO	0.13	0.05
MgO	0.82	0.09
CaO	0.56	0.06
Na_2O	0.24	0.04
Ignition loss	3.32	0.21

CONCLUSIONS

In present research work, three different siliceous agriculture wastes were thermally degraded. General thermal degradation behavior of all treated and untreated samples of rice husk, wheat husk and bagasse was similar. At 400°C, weight loss of three biomasses (R2, W2 and B2), treated with HCl at room temperature, is maximum. At 800°C, again the weight loss of samples R2, W2 and B2 is maximum. To extract silica from SAW, it is better to soak in HCl instead of boiling before calcination. Thermal degradation allows the formation of silica at 650°C just in 1hour. Hence energy saving is one of the important benefit of thermal degradation. Residual weights at 800°C in all cases are higher indicating that rate of calcination should be less than 10°C/min.

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