



## Characterization and Evaluation of Thermodynamic Parameters for Egyptian Heap Fired Rice Straw Ash (RSA)

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### Abstract

The composition of the studied ash was confirmed by elemental analysis, IR, XRD spectra, and thermal data (TG & DTA). These analyses were used to determine thermodynamic parameters such as the activation energy ( $\Delta E_a$ ), enthalpy change ( $\Delta H^*$ ), entropy change ( $\Delta S^*$ ) and free energy change ( $\Delta G^*$ ) related to the thermal decomposition process were calculated. Analytical reactions were also used to evaluate the composition of the ash.

**Keywords:** Rice Straw Ash (RSA), Thermal analysis, Thermodynamics of RSA, Chemical characterization of RSA

### 1. Introduction

All agricultural residues are biological forms of renewable energy, rice straw is considered to be the most important of such residues. From this point of view, in most rice producing countries, it is one of the major by-products from rice production process. The husk, consisting mainly of ligno-cellulose and silica, is a poor animal feed source and its main usefulness is its energy content. (James J., 1986; Feng Q., 2004; Smith R.G., 1986; Dass A., 1984; Birch G.G., 1975). The utilization of rice straw as a source of energy production is urgently needed in Egypt while the firing residue is marketable silica. After using any agricultural residue as an energy source (either by direct firing or by gasification) a certain amount of ash consisting mainly of silica and carbon remained. This amount depends mainly on the type of the used agricultural residue and the working conditions such as firing temperature and amount of air used. This also determines the crystalline state of the produced silica and hence its reactivity. (Loehn R.C., 1974; Hobson P.N., 1977; Hicks P.A., 1991; Bewick M.W., 1980). The aim of this work is to study the composition of the ash remained after firing rice straw, this was done using different analytical methods.

### 2. Experimental

Three samples of (RSA) were collected from three different places in delta sample I, sample II, and sample III. Moisture content of (RSA), combustible organic matters and water soluble matters were determined. The composition of the ash was confirmed by elemental analysis, IR and XRD spectra. The thermal studies were carried out using DTA-50,

TGA-50, Shimadzu Thermogravimetric analyzer (Japan), with a rate of heating 10 °C / min. Effects of different concentrations of dil. HCl and NaOH solutions on ash were also studied.

### 3. Results and Discussion

#### 3.1 Characterization of RSA by physical methods of analysis.

##### 3.1.1 Determination of the moisture content of heap fired RSA

The moisture content of the RSA samples was determined by heating the samples at 120 °C till constant weight. The moisture was found to be 3.2 % sample I and 3.6 % for each of samples II and III.

##### 3.2 Chemical analysis of RSA

Chemical analysis of the RSA samples was carried out by the recommended methods. Table 1, indicates that silicon dioxide constitutes over 65 % of the total mass of RSA. Other metallic oxides present are CaO, Al<sub>2</sub>O<sub>3</sub>, MgO in addition to traces of iron oxides.

##### 3.3 Thermogravimetric Analysis (TGA) of RSA

The TGA curves of the three samples display similar behavior, each curve comprises three main regions. The first region within the range 20-200 °C corresponds to the removal of the moisture content of the samples (3.2 – 3.7 %) together with some volatile materials. These later are higher in sample III than in the other two samples. The second stage within the 200-550 °C range amounts to (5.2 – 11.3 %) would correspond to the burning of the carbonaceous material in the samples. The last step in the range (550 - 800 °C) is of low mass (1.4 – 2.6 %) and may represent the combustion of carbon that was firmly adsorbed on the surface of the solid materials remaining or the volatilization of some metal oxides (Kenawy I.M.M., 1994; Chetterjee P.K., 1968).

##### 3.4 Differential Thermal Analysis (DTA) of RSA

Table 3, gives the results of the differential Thermal analysis of the tested heap fired rice straw ash samples.

The DTA curves of the three samples were found to comprise three to five peaks. Comparing these results with those of TGA (table 2), it is evident that the three steps in the TGA curves correspond to steps 1, 2 and 3 in the DTA experiment. The other peaks would be due to phase transformations occurring in the solid samples during the rise of temperature (Coats A.W., 1964).

The DTA curves can be used to calculate some thermodynamic parameters of the thermal changes occurring in the tested samples during firing. For this propose the following relations were used (Paunovic M., 2005).

$$\ln K = \ln A - (E_a / RT) \quad (1)$$

where:

K: is the rate constant.

A: the frequency factor.

R: the gas constant.

E<sub>a</sub>: the activation energy.

Plot of ln K as a function of 1 / T is a linear relationship; E<sub>a</sub> was determined from the slope of this plot.

The following relation can be used to calculate ΔH (Paunovic M., 2005).

$$\ln (K / T) = \ln (KB / h) + (\Delta S / R) - (\Delta H / RT) \quad (2)$$

in which:

KB: is the Boltzman constant.

h: Planks constant.

Plot of ln (K / T) vs. 1 / T gives a linear relationship and ΔH can be determined from its slope. Results obtained are summarized in table (3); the abnormal values shown in this table may be ascribed to some side reactions as the combustion of carbon and some phase transformations of silica present in the solid phase (Coats A.W., 1964).

##### 3.5 IR spectral analysis

The IR spectra of RSA samples together with samples subjected to some chemical treatments were recorded in the solid state as KBr discs. The bands of diagnostic importance are collected in table (4), for sake of comparison results for IR spectra of silica samples from the literature are also depicted. The samples involved in the present study are as in scheme (1). The data reveal the existence of the bands characteristic of silica in all samples at 3480 – 3200 cm<sup>-1</sup> (νO-H), 2430 – 2330 cm<sup>-1</sup> (νSi-H), 1100 – 1030 cm<sup>-1</sup> (SiO<sub>2</sub> lattice vibration), 800 – 780 cm<sup>-1</sup> (Si-O-Si stretching), and 480 – 460 cm<sup>-1</sup> (Si-O-Si bending). The vibration modes for the water molecules displayed as brood bands with strong intensity at

3445 – 3425  $\text{cm}^{-1}$  ( $\gamma\text{H}_2\text{O}$ ), 1630 – 1620  $\text{cm}^{-1}$  ( $\delta\text{H}_2\text{O}$ ) and 980 – 832  $\text{cm}^{-1}$  ( $\nu\text{H}_2\text{O}$ ). The various chemical treatments did not affect much the form of silica present in RSA, which is similar to previous observations (Paunovic M., 2005; Mozzi R., 1970).

The leaching of silica from RSA with NaOH and then the precipitation of the extracted silica with HCl or  $\text{H}_2\text{SO}_4$  yield most probably a mixture of silica and silicic acids which is gathered from the IR spectra. The bands in the region 2900 – 1750  $\text{cm}^{-1}$  can be ascribed to some organic materials formed during the firing of RS adsorbed on the RSA. These bands disappeared from the samples of silica obtained by leaching with NaOH and precipitation with acid (6,7) as well as from the residue remaining after leaching. This reflects that such materials were turned soluble during the chemical treatment. The IR bands of unwashed and washed RSA samples (1-5) are quite comparable with those reported for amorphous silica present in natural sources. This reflects that silica present in RSA or samples washed with NaOH, HCl, or  $\text{H}_2\text{O}$  is in the amorphous form which is actually the most reactive form of silica.

### 3.6 X-Ray Diffraction analysis (XRD)

The X-ray patterns of the three RSA samples showed no characteristic lines, indicating that the solid contents of the samples are existing mainly in an amorphous form.

### 3.7 Chemical characterization of the RSA samples

#### 3.7.1 Amount of water soluble matters from the rice straw ash (RSA)

Results of the tests conducted to detect the amount of water soluble matters in (RSA) are given in table (5). The results indicate that the medium turned alkaline on leaching and the time of stirring has little effect on the amount dissolved. This donates that an equilibrium is readily established between the solid and solution phases. The amount of leached compounds increased obviously on boiling the reaction mixture.

#### 3.7.2 Effect of dilute hydrochloric acid on RSA

The effect of treatment with dilute hydrochloric acid (10 %) on the RSA as has been noticed in tables (6a and b) that RSA was affected by loss 14-29 % from its initial weight according to the complete loss of alkali oxides.

#### 3.7.3 Effect of sodium hydroxide solution on RSA

The solubility of amorphous  $\text{SiO}_2$  in sodium hydroxide solution is controlled by many factors, such as sodium hydroxide solution concentration, and temperature; the effect of such factors and the obtained results are summarized in tables (7-9).

##### 3.7.3.1 Effect of sodium hydroxide solution concentration

Tables (7a and b) gives the results for this study, from which the suitable NaOH solution concentration found is 0.8M. In such a solution about 70.0 % of the total weight of RSA was solublized. This ratio would be about 95.0 % of the total  $\text{SiO}_2$  found in rice straw ash.

##### 3.7.3.2 Effect of treatment duration with sodium hydroxide solution

To determine the optimum time period for leaching RSA by 0.8M solution of sodium hydroxide, different time periods (1, 2, 4, and 5 hrs) for leaching were conducted as seen in table (8). These tables clears that it is sufficient to boil RSA in 0.8 M NaOH solution for 2 hrs. to dissolve the maximum amount of solid matter from it.

##### 3.7.3.3 Effect of temperature

This test was carried out to determine the suitable temperature for the leaching of RSA by 0.8M NaOH solution. Table (9) represents the results obtained. This table shows that more solids are dissolved with temperature rise and the maximum amount dissolved is reached with boiling for two hours.

## 4. Conclusion

Firing of agricultural residues to produce heat energy leads to char production which is the firing residues. This char is a mixture of unburnt carbon, some organic matters, metallic oxides and silicon dioxide. While the amount of silicon dioxide present in the char is dependent upon the type of the agricultural residue, the amount of unburnt carbon is determined by air availability and firing temperature. Silicon dioxide present in the char is either crystalline or amorphous depending mainly upon the firing temperature of the agricultural residue.

Characterization of rice straw ash was done using different methods such as; Chemical composition measurements which showed that RSA constitutes silicon dioxide (over 65% ) of the total mass of RSA, other metallic oxides present are CaO (about 2.4 %),  $\text{Al}_2\text{O}_3$  (1.78%), MgO (3.11% ) in addition to traces of Ferric oxide. Loss on ignition at 1000 °C was found to be about 9.71 %, this includes the moisture, organic matters in addition to the carbon present in the heap fired RSA.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) for heap fired rice straw ash were

undertaken. The obtained results indicated that the ash contains about 3.5 % of its mass as moisture while the amount of organic matters and carbon present was 9.5 %, this is compatible with the results of heating heap fired RSA at 120 °C for 2 hrs. followed by burning at 900 °C till a constant weight.

IR analysis, and XRD measurements have a great importance in detecting the chemical bonding and modes of vibrations between atoms present in the tested samples. These measurements were carried out on different samples from RSA. The obtained results were then compared with reference samples in the literature. This showed that the ash contains amorphous silica as gathered from the band rich IR patterns; which means that the silica present is in its most active state.

Rice Straw Ash samples were also characterized through chemical treatment; with water, hydrochloric acid, and caustic soda. Determination of the amount of water soluble matters in the rice straw ash (RSA) were conducted through leaching of heap fired RSA by either cold water or by boiling water. Leaching with cold water removed about 11.5 % from the ash. During leaching the pH value of the medium was almost constant at 9.2 which means that the soluble matters are mainly alkali's oxides while leaching of heap fired RSA by boiled water removed about 25 % of its initial mass. This means that the mass of soluble matters was almost duplicated on boiling. This effect was found to be due to that the alkali oxides that dissolved in water affect the dissolution of some SiO<sub>2</sub> from RSA. Effect of diluted hydrochloric acid upon RSA was also studied, about 23.0 % of the total mass of the heap fired RSA was leached in cold 10 % HCl solution while about 70 % of the silica present in RSA was leached by sodium hydroxide. The amount of silica leached increased with increasing the concentration of NaOH solution, duration of treatment, and the temperature of the treatment media.

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Table 1. Chemical composition of RSA

Constituents%	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO/CaO	SO <sub>3</sub>	Loss on ignition	Total
Sample I	65.92	1.78	0.2	2.4	3.11	0.69	9.78	83.81
Sample II	65	1.7	0.19	2.5	3.1	0.7	9.9	83.8
Sample III	66	1.9	0.18	2.4	3.2	0.8	9.8	85

Table 2. TGA analysis of RSA samples

Sample No.	Step(1)		Step(2)		Step(3)	
	Range (°C)	Wt. Loss (%)	Range (°C)	Wt. Loss (%)	Range (°C)	Wt. Loss (%)
I	17.29-201.02	4.86	202.52-544.79	11.317	544.79-799.69	1.425,
II	19,07-186.56	3.72	188.1-475.16	5.236	478.69-799.57	2.512,
III	19.31-158.88	7.34	159.97-480.5	10.227	480.99-799.4	2.643

Table 3. Differential thermal analysis of the tested heap fired rice straw ash

Sample Peak	RSA I			RAS II					RSA III				
	1	2	3	1	2	3	4	5	1	2	3	4	5
ΔH kj/m	11.3	15.9	5.5	5.53	68.8	14.5	10.7	6.73	37.1	7.75	67.8	11.2	22.9
ΔEa kj/m	104	16.6	74.9	2.25	42.3	6.7	8.87	6.3	2.6	26.2	10	15	20
ΔS kj/m	-116.5	-62.31	-1103	-108.6	318	-5208	-111.1	-170.	-87.02	-302	-102.8	-139.4	-632
ΔG kj/m	39632	239429	75495	48.7883	163958	32233	717057	122826	38488	155405	631252	915003	45272

Table 4. IR spectra of RSA samples

Sample	IR spectral bands of diagnostic importance										
	440	850	872	905	922	939	1000	1035	1430	1490	-
L	440	850	872	905	922	939	1000	1035	1430	1490	-
C	440	570	820	860	925	940	950	-	-	-	-
H	453	706	796	906	935	966	1020	1034	1445	1610	362
S	463	583	667	720	775	832	898	980	1007	1040	340
1	463	791	1085	1417	1631	-	-	-	-	-	342
2	463	793	1088	1476	1622	1728	1986	2353	2851	-	342
3	465	797	1075	1484	1562	1772	1866	2333	2854	-	342
4	467	798	1060	1419	1631	1868	-	2337	-	-	342
5	480	791	1055	1485	1630	1864	2016	2319	2855	-	344
6	278	-	877	912	-	-	1000	1135	1424	1631	363
7	404	-	872	-	-	951	-	1050	1476	1630	362
8	475	621	-	-	790	-	-	-	-	1097	342
9	471	-	-	-	787	-	-	-	-	1098	344
10	462	-	668	-	790	-	-	-	2428	1038	342
	Si-O -Si	Si-O- Si	SiO <sub>2</sub> lattice	-	H <sub>2</sub> O bendin	-	-	Si-H str.,	-	-	H <sub>2</sub> O

L- Larnite  $\beta$  Ca<sub>2</sub>SiO<sub>4</sub>

C- Calcio olivine  $\gamma$  Ca<sub>2</sub>SiO<sub>4</sub>

H- Hillebrandite Ca<sub>2</sub>SiO<sub>3</sub> (OH)<sub>2</sub>

S-Na<sub>2</sub>SiO<sub>3</sub>.5H<sub>2</sub>O (sodium metasilicate reference sample)

1) Ash sample.

2) Ash washed in 800 ml-distilled water by boiling for 2 hrs.

3) Ash treated with 10 % HCl solution by boiling for 2 hrs.

4) Ash (control fired at 500 °C for 4 hrs) and washed in 800 ml distilled

5) Ash (control fired at 500 °C for 4 hrs), treated with 10 % HCl solution and boiling for 2 hrs.

6) CaO sample prepared by calcination of lime (at 1000 °C for 1 hr ).

7) CaO sample prepared by calcination of sugar cane waste.

8) H<sub>2</sub>SiO<sub>4</sub> prepared from the reaction (Na<sub>2</sub>SiO<sub>3</sub>+H<sub>2</sub>SO<sub>4</sub>).

9) H<sub>2</sub>SiO<sub>4</sub> prepared from the reaction (Na<sub>2</sub>SiO<sub>3</sub> + HCl).

10) Carbon residue from the reaction between RSA and 0.8M NaOH, boiling for 4 hrs.

Table 5-a. Leaching of RSA with cold water

Time/m	Heap fired ash								C(500)	C(700)
	5	10	15	30	45	60	120	180	120	120
PH	9.3	9.33	8.96	9.23	9.28	9.21	9.16	9.3	8.81	9.1
Loss%	16.5	17.0	14.4	14.8	15.4	16.4	15.0	15.0	10.0	9.0

C(500): rice straw ash obtained when burning rice straw at 500 °C.

C(700): rice straw ash obtained when burning rice straw at 700 °C.

Table 5-b. Leaching of RSA with boiled water

Time/m	40	75	120	120	120
PH	8.44	8.46	8.07	8.40	8.30
Loss%	30.0	26.3	27.4	30.0	24.6

pH of distilled water used = 7.6

Table 6-a. Leaching of RSA with 10 % HCl cold acid solution

Heap fired ash						C(500)	C(700)
Time/m	10	30	40	60	120	120	120
Loss%	24.5	26.5	22.5	21.0	23.0	29.0	14.4

C(500): rice straw ash obtained when burning rice straw at 500 °C.

C(700): rice straw ash obtained when burning rice straw at 700 °C.

Table 6-b. Leaching of RSA with 10% HCl acid solution with boiling

Heap fired ash				C(500)	C(700)
Time/m	60	120	180	120	120
Loss%	14.5	23.0	25.6	29.0	19.14

Table 7. Effect of NaOH solution concentration

i) Washed ash					
NaOH Conc.	0.08M	0.2M	0.4M	0.8M	1.6M
Loss%	59.4	57.6	64.4	70.8	72.2
ii) Unwashed ash					
Loss%	59.6	66.6	69.4	71.2	72.8
iii) Control fired ash (at 500 °C)					
Loss%	84.06	84.48	83.4	68.97	

Table 8. Effect of treatment duration

i) Unwashed RSA in 0.8M NaOH at boiling				
Time/hrs	1	2	4	5
Loss%	73.2	77.6	71.2	77.4
ii) Washed RSA				
Loss%	64	70.4	70.8	67
iii) Control fired ash (at 500 °C)				
Loss%	83.4	83.4	83.4	83.45

Table 9. Effect of temperature

i) Boiling in 0.8M NaOH solution				
Time/m	1	2	4	5
Loss %	74	77.6	71.2	77.4
ii) Heating at 60 °C				
Loss %	44.6	50.4	57.6	60.2
iii) Heating at 40 °C				
Loss %	28.2	30.4	36.4	37.6

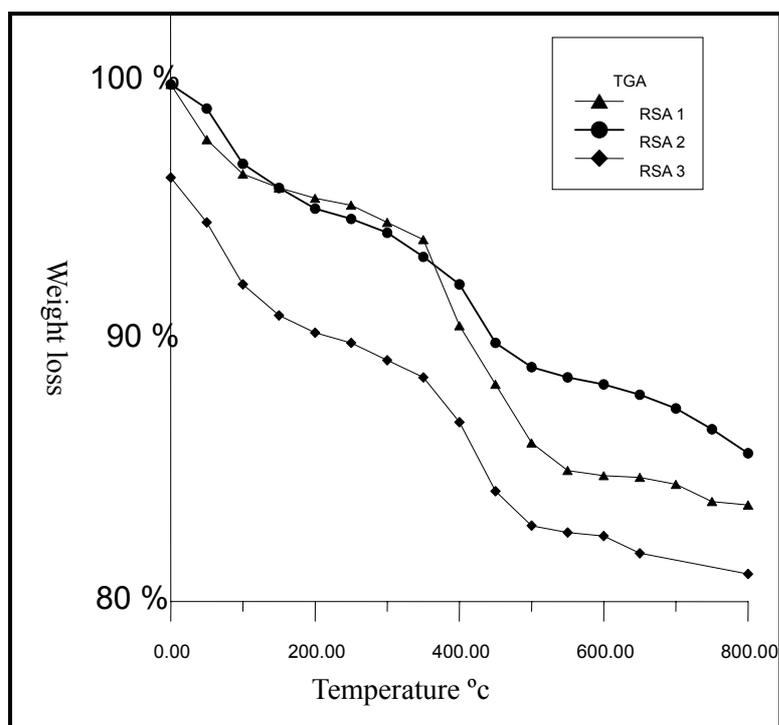


Figure 1. TGA curves for three different RSA samples