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A STUDY ON THE THERMAL DESTRUCTION OF RICE HUSK IN AIR AND NITROGEN ATMOSPHERE

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The methods of X-ray analysis, infrared spectroscopy, differential thermal analysis and scanning electron microscopy were used in this study. The objects of the experiments were rice husk obtained during processing of rice, variety Krasnodarski 424. The rice husk was burnt in air and in non-oxygen medium at several burning temperatures. The color of the oxidized product was stipulated by the burning temperature. The X-ray analysis showed that the amorphous SiO_2 present in the rice husk begins to crystallize in the form of α-cristobalite at 850°C. Using differential thermal analysis, the thermal destruction of rice husk was studied in air and nitrogen media and the initial and final temperatures of the process were determined. The silica distribution was examined by scanning electron microscopy and infrared spectroscopic techniques.

Keywords: *DTA, rice husk, thermal destruction, white and black ash, X-ray analysis*

Introduction

According to FAO [1], about 500 mln tons of rice are processed in the world which give ca. 100 mln tons rice husk. Thus, its utilization poses serious ecological and technological problems. Rice husk has abrasive structure and low content of nutritious components which makes them unsuitable for use as food for livestock. Due to the high content of lignine and ash, they are unsuitable raw material for paper production industry. Rice husk cannot be used as natural fertilizer since it is resistant to moisture and oxygen and soil humification. They are usually burnt in open air, thus releasing large amounts of hazardous substances in the atmosphere [2].

That motivated the efforts of many researchers to find ways for utilization of this widely spread waste material. It is well known that rice husk contain inorganic part (mainly SiO_2) and organic part consisting of cellulose, lignine and hemicellulose [3–5]. Due to the high content of silicon dioxide (13–29%), a number of materials – silicon dioxide [6-10], silicon carbide [11, 12], silicon nitride [13], silicon [14, 15], cordierite [16], lithium-aluminium ceramics [17], fire-resistant materials [18], etc., can be synthesized from it after proper thermal or chemical treatment. The burning of rice husk in air is known to give solid residue containing mainly SiO_2 or mixture of SiO_2 and carbon [19–21]. The solid residue has large internal area and can be used as adsorbent [22–25] or filler for inorganic or polymeric composite materials [26–32].

The increasing interest to rice husk requires complete investigation of the processes of thermal destruction using several analytical methods. Some data obtained by individual methods have been published in the literature but there are no comprehensive studies in this field. This motivated the study reported by the present paper.

Experimental

Materials

The present study was carried out with rice husk obtained during processing of rice variety Krasnodarski 424 grown in Bulgaria. This kind of rice contains 17.8% husk. They are arc-shaped and size approximately: 8 mm length, 2–3 mm width and 0.10–0.15 mm thickness. The husk contain 74.5% organic matter (cellulose, hemicellulose and lignine) and water, and the rest is inorganic matter containing 20% SiO_2 and 5.5% mixture of the following oxides: CaO, Fe_2O_3, MgO, Al_2O_3, Na_2O, K_2O, MnO_2, as well as traces of Cu and Pb.

The objects of the experiments were three kinds of samples:

- raw rice husk (RH), preliminarily washed to remove mechanical impurities and dried at 120°C;
- husk oxidized at 650°C and 1000°C in air – white ash (WRHA);
- husk carbonized at 1000°C in nitrogen – black ash (BRHA).

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Table 1 Contents of SiO_2 and C, and particle size of thermally treated rice husk

Thermally treated Rice husk	Contents/mass%		Average particle size/μm
	SiO_2	C	
Oxidized at 650°C	91.63	2.84	4.5
at 1000°C	94.47	–	5.7
Carbonized at 1000°C	54	40.46	3.6

Methods

The husk was studied by X-ray analysis, infrared (IR) spectroscopy, differential thermal analysis (DTA) and scanning electron microscopy (SEM).

The X-ray analyses were carried out by the method of powder diffraction using X-ray apparatus equipped with goniometer URD-6 (Germany) with cobalt anode and K_α emission.

The IR studies were performed on a spectrophotometer SPECORD-75 (Carl Zeiss-Jena, Germany) in the interval 400–4000 cm^{-1} at resolution of 1 cm^{-1}.

The DTA experiments were performed on a derivatograph OD-102 (MOM, Hungary) by heating to 1000°C at a rate of 10°C min^{-1}.

The average size of the particles was determined by SEM. The micrographs were taken using scanning electron microscope Tesla BS 340 (Czech Republic).

The SiO_2 content in the solid residue was determined after treatment with hydrofluoric acid and the carbon content – by automatic gas analyzer Carlo Erba 1104 (Italy).

Results and discussion

Physico-chemical characteristics of white and black ash

For the determination of the physico-chemical properties of WRHA, raw rice husk was burnt in air at several temperatures: 500, 600, 650, 700, 800, 850, 900, 1000, 1100 and 1200°C. The color of the oxidized residue depends strongly on the burning temperature. The powder was almost black up to 500°C since the organic matter had not been burnt totally yet. At temperatures 600–700°C, the initial rice husk sample transformed into grey-white ash with varying intensity due to the presence of non-oxidized carbon. White microcrystalline powder with high content of SiO_2 was obtained at higher temperatures when all the carbon had been removed.

Table 1 presents some of the basic characteristics of the amorphous powder obtained at 650°C and the crystalline powder obtained at 1000°C. It was found that the burning of raw husk in air gives oxidized residue containing more than 90 mass% SiO_2. For comparison, data on husk burnt in nitrogen atmosphere at 1000°C are also shown. The carbonization of RH in nitrogen medium at 1000°C gives finely dispersed black powder resembling active carbon due to the content of amorphous carbon.

X- ray analysis

Since the raw and the thermally treated rice husk can be used as components in composite materials [32], it is important to know what structure changes they undergo during heating. The determination of the temperature up to which the powder is amorphous is significant because the crystalline product has lower reactivity than the amorphous one. Using X-ray analysis, the change of rice husk structure caused by their burning at different temperatures in oxidative and inert media was assessed (Figs 1 ways pattern a–f).

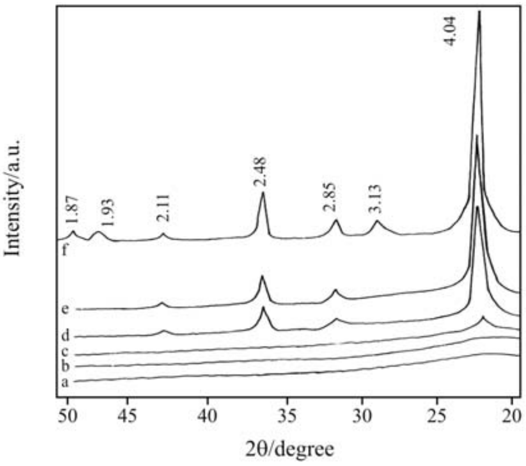

Fig. 1 X-ray diffraction patterns of: a – rice husk burnt in nitrogen at 1000°C; b – f – rice husk burnt in air at 800, 850, 900, 1000 and 1200°C, respectively

The studies showed that the burning of rice husk at temperatures up to 800°C either in air or in inert medium gives amorphous product. The sample oxidized at 850°C indicated slight crystallinity. The diffractogram presented in Fig. 1c shows a distinguishable peak (*d*= 4.04 Å) corresponding to the high – crystalline phase of silica – α-cristobalite, while at 900°C (Fig. 1d), the patterns had four peaks characteristic for α-cristobalite (*d*=4.04; 2.85; 2.48; 2.11 Å). The same peaks were observed at 1000°C (Fig. 1e) but with higher intensity, i.e. the increase of burning temperature facilitates the crystallization of silica in WRHA. All the seven peaks registered at 1200°C (Fig. 1f) are characteristic also for α-cristobalite with traces of tridymite. Quartz was not detected.

The carbonization of rice husk in nitrogen atmosphere at 1000°C (Fig. 1a) gives fully amorphous product in confirmation to earlier reports [11, 12], while that obtained at the same temperature in air showed varying intensity and the integral area of the highest peak of cristobalite (at d=4.04 Å), depending on the time of isothermal soaking (Fig. 2).

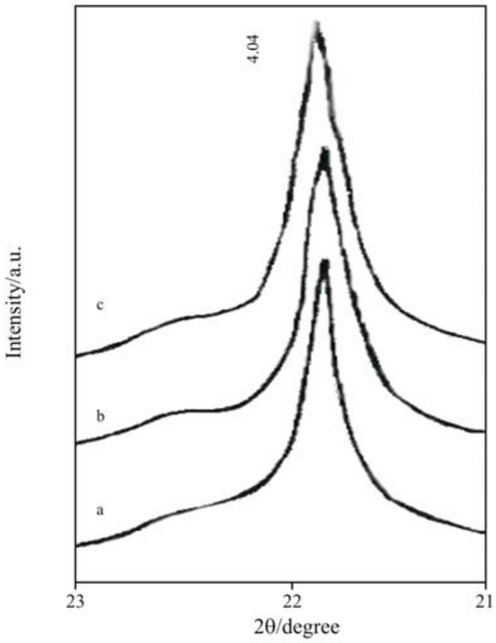

Fig. 2 Effect of isothermal soaking at 1000°C: a – 20, b – 40, c – 60 min on the extent of crystallization of silica

As can be seen from Fig. 2, the amount of SiO_2 crystallized in WRHA as α-cristobalite increased with the increase of isothermal soaking period. The ratio between the intensities of the highest peaks of α-cristobalite (at d=4.04 Å) obtained at 20, 40 and 60 min isothermal soaking was 0.79:0.89:1.00, respectively, where the peak with the highest intensity was assumed to be 1.00. The peak intensity after 60 min isothermal soaking at 1000°C was found to remain the same, which means that the process of rearrangement and crystallization of the solid residue had finished.

Infrared spectroscopy

The studies on husk structure using IR spectroscopy were carried out with three kinds of samples (Figs 3a–c): raw rice husk (Fig. 3a), husk burnt in air at 650°C (Fig. 3b), and husk carbonized in nitrogen medium at 1000°C (Fig. 3c).

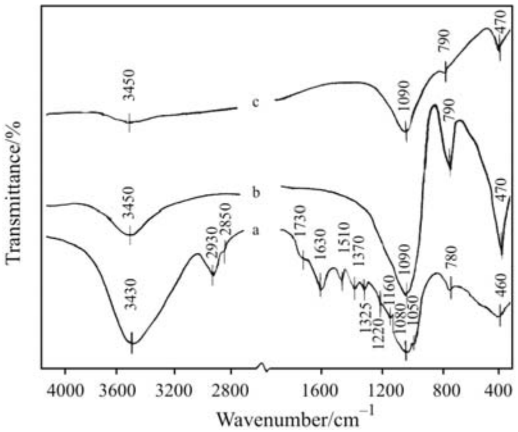

Fig. 3 IR spectra of the samples studied: a – raw rice husk, b – rice husk burnt in air, c – rice husk burnt in nitrogen medium

The absorption bands observed in rice husk IR spectra were attributed to physically adsorbed water, lignine functional groups, cellulose and hemicellulose, as well as the inorganic component in husk composition

Thus, the wide and intense absorption band with maximum about 3430 cm^{-1} can be attributed either to the valent vibrations of the O–H bond in water molecules bonded by hydrogen bonds, or to OH groups present in cellulose, hemicellulose and lignine [33]. The same authors [33] state that the absorption bands observed in the IR spectrum of non-treated husk at 1370, 1325, 1220 and 1050 cm^{-1} can be related to the OH groups in lignine and polysaccharides forming husk structure. The band at 1640 cm^{-1} results from both the deformation vibrations of the water molecules (δ-H_2O) and the presence of C=C bonds in the organic component. These bands disappear in the IR spectra of the samples thermally treated either in air or in inert medium. The intense absorption band at 2930 cm^{-1} and the less intense band at 2850 cm^{-1} can be attributed to the asymmetric (ν_{as}) and symmetric (ν_s) valent vibrations of the C–H bonds in $-CH_3$ and $-CH_2$ groups in the structures of lignine, cellulose and hemicellulose, respectively. The band at 1730 cm^{-1} was related to the C=O bonds in the aldehyde groups of hemicellulose while that at 1510 cm^{-1} is characteristic for the vibrations of the C=C bonds in the aromatic rings of lignine. The absence of absorption bands at 1510 and 2930 cm^{-1} in thermally treated samples indicates for the full destruction of the organic component in rice husk [34]. The triplet in the region 1000–1200 cm^{-1} was considered to result from superposition of vibrations of the C–OH bond and Si–O bond in the siloxane groups.

The intense band at 1050–1100 cm^{-1} with maximum at 1080 cm^{-1} corresponds to valent vibrations of silicon-oxygen tetrahedrons – ν_{as} (SiO_4) [35, 36]. The presence of such an absorption band was considered enough to suggest that silicon in husk is bonded in silicon-oxygen tetrahedrons [37]. The fact that this absorption band was quite intense in all the three samples spectra clearly showed that the bond Si–O–Si in the inorganic matter of the initial and thermally treated husk remained intact. On the other hand, it would not be absolutely correct to relate the band at 1080 cm^{-1} to the bond Si–O–Si only since the main valent vibrations of the C–OH bond of cellulose are also in that IR region. The comparison of the intensities of this band for the raw and thermally treated husk showed that it was slightly higher than the former. As it has been mentioned above, the higher intensity at 1080 cm^{-1} observed in the spectrum of the raw rice husk was probably due to superposition of the valent vibrations of the C–OH bond in the interval 1000–1200 cm^{-1} and the valent vibrations of the Si–O bond.

The weak absorption bands at 780 and 460 cm^{-1} registered in the spectrum of the raw husk were also attributed to their silicon-oxygen component [37]. As can be seen from Fig. 3, both bands were much more intense in the spectrum of oxidized husk which contain more than 90% SiO_2, and were shifted to 790 and 470 cm^{-1}, respectively. The presence of an absorption band at 780–790 cm^{-1} can be explained with the symmetric valent vibrations (ν_s) of the Si–O bonds in the silicon-oxygen tetrahedrons (SiO_4) [37]. The absorption bands observed in the low-frequency part of the spectrum can be attributed to deformation vibrations (δ_{as}) of the Si–O bonds.

Derivatographic studies

The development of various technological methods for utilization of rice husk by biological or thermal decomposition can not be accomplished without profound studies on the processes of their thermal destruction by DTA-analysis. From thermogravimetric calculations based on the data obtained from DTA, the kinetic characteristics of the destruction processes can be determined, as it has been already reported earlier [38, 39].

It is known [40–42] that the thermal destruction of rice husk has three stages: drying (40–150°C), removal of volatile organic components (215–350°C) and burning of carbon (350–690°C).

The present derivatographic studied were carried out under the following conditions:

- in static air. Under heating, first the physically adsorbed water was released (5%), followed by the burning of the organic components to obtain solid residue (26% containing mainly SiO_2);
- the second method for treatment is carbonization of the raw rice husk in nitrogen medium flowing at 25 cm^3 min^{-1}. First, the physically adsorbed water was released, followed by pyrolysis of the organic matter to obtain solid residue (43%) containing mainly carbon and silica;
- the rice husk carbonized in nitrogen as described above are then oxidized in air to burn the carbon component and obtain 51% solid residue.

In further discussion, the samples treated by the three methods described above will be denoted as a, b and c, respectively (Fig. 4).

Comparing the derivatograms of the samples treated by the first and second method (TG curves a and b, Fig. 4), it can be seen that the processes of thermal destruction in nitrogen and air were the same up to 200°C and then were parallel up to 400°C.

The DTA analysis of rice husk treated in oxidative medium (Fig. 4a) showed that the physically adsorbed water was released in the temperature interval 80–180°C which was indicated by the 5% mass loss. The process of thermal destruction began at 220°C and ended at 640°C with 74% mass loss. The mass loss at 270°C was 10% and at 430°C – 50%. The processes of thermal destruction proceeded with maximum rate at 320°C in air and 360°C in nitrogen.

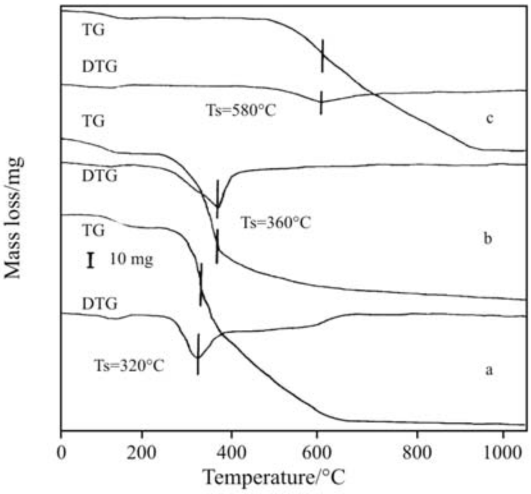

Fig. 4 TG and DTG curves of samples at: a – burning in air, b – pyrolysis in nitrogen, c – oxidation of the carbonized residue in air

The DTA and TG curves of rice husk carbonized in nitrogen medium (Fig. 4b) showed that the region with the highest pyrolysis rate was from 300 to 360°C, and above this temperature the rate gradually decreased. The mass loss at 480°C was 50% and up to 670°C the process practically ended – the mass loss was 55% (solid residue 45%) and further heating to 1000°C gave only another 2% mass loss (down to 43% solid residue). Therefore, it can be concluded that the process of carbonization ends at 670°C and further increase of temperature does not give significant change in samples mass.

The DTA and TG curves of carbonized residue from rice husk additionally oxidized in air are presented in Fig. 4c. About 2.5% physically adsorbed water was released up to 120°C and all the water was released up to 150°C. The volatile substances were released in the temperature interval 120–420°C – mainly CO_2, CO, H_2 and CH_4. Oxidative processes began above 420 and ended at 870°C in air. The DTG curve clearly shows that the highest thermal destruction rate was observed at 580°C. The initial sample lost 49% of its mass as a result of the oxidative burning.

Electron microscopy studies

Figures 5a–c shows scanning electron micrographs of the three samples studied and Fig. 6 – micrograph of raw rice husk.

As can be seen from these micrographs, the external relief of raw and thermally treated husk is built from interconnected dome-shaped regions. After burning in air or inert medium (Figs 5a, b), the husk surface did not change compared to the raw husk (Fig. 6). Undoubtedly, the preservation of the shape was due to the uniform distribution of SiO_2 on its surface. This fact can be explained with the assumption that the outer protective layer of the husk is formed from silicon dioxide only, the existence of which has been proved by the IR spectroscopy studies. It can be related also to the basic biological role of the husk to protect the grain from mechanical damage and retain water within it.

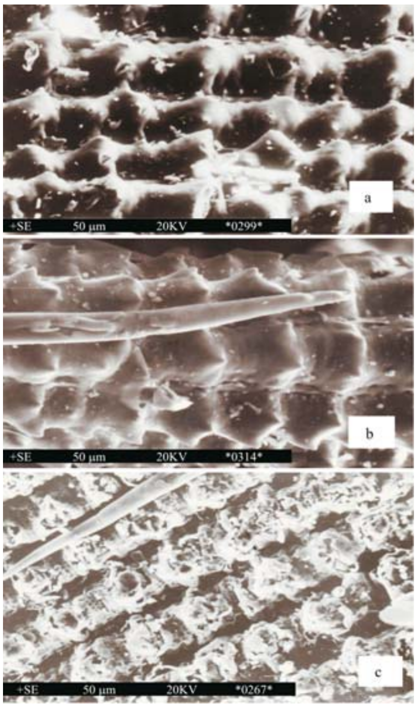

Fig. 5 Micrographs of: a – oxidized rice husk, b – carbonized rice husk, c – carbonized rice husk further burnt in air

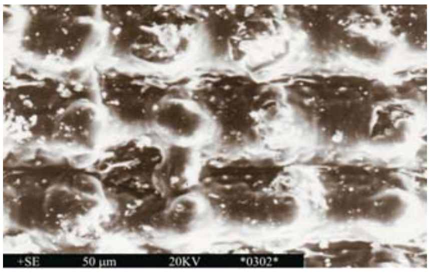

Fig. 6 Micrograph of raw rice husk

It can be seen for the oxidized product obtained by further burning of the pyrolysis product in air that the ‘domes’ were partly destructed due to difficulties in the release of volatile components stipulated by the strong silicon-oxygen carcass (Fig. 5c).

Conclusions

In summary, we can conclude that the thermal destruction of rice husk began at 220 and ended at 640°C in air and began at 240 and ended at 670°C in nitrogen medium, respectively. The burning of rice husk in oxidative medium at temperatures 650–1000°C gives fine powder with particle size 4–6 μm. WHRA obtained at 650°C contain 91.63% SiO_2, while these obtained at 1000°C contain almost 95% SiO_2 (94.47% SiO_2). The crystallization of silicon dioxide starts at 850°C where SiO_2 crystallizes directly in its high-temperature modification – α-cristobalite.

Studies using infrared spectroscopic techniques and scanning electron microscopy (SEM) revealed that silica is concentrated mostly in the external protective layer of the rice husk. By this reason the micrographs of the thermally treated husk did not change significantly compared to that of raw rice husk.

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