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Thermal degradation of rise husks: Structure, morphology, thermal and kinetics characteristics

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ABSTRACT

Rice husks are an important by-product of rice milling process and are major waste product of the agricultural industry. They have now become a great source as a raw biomass material for manufacturing value-added silicon composite products, including silicon carbide, silicon nitride, silicon tetrachloride, magnesium silicide, pure silicon, zeolite, fillers of rubber and plastic composites, adsorbent and support of heterogeneous catalysts. The bulk and true densities of raw rice husks (RRH) with different moisture and sizes were determined. The rice husk was subjected to pyrolysis in fluidized-bed reactor in air or nitrogen atmosphere. The controlled thermal degradation of the rice husks in air or nitrogen leads to production of white rice husks ash (WRHA) and black rice husks ash (BRHA) respectively. The products obtained were characterized by X-ray powder and thermogravimetric analysis, IR-spectroscopy, scanning electron microscopy and nitrogen adsorption. WRHA contains almost pure (≥95mass %) silica in a hydrated amorphous form, similar to silica gel, with high porosity and reactive surface OH groups. BRHA contains different amounts of carbon and silica in amorphous form with high specific surface area and porosity. On the basis of non-isothermal heating of raw rice husks in air or nitrogen media was established, that the kinetics of the pyrolysis process were best described by the equation of Ginstling-Brounshtein, valid for diffusion-controlled reactions, starting on the exterior of spherical particles with uniform radius. The values of activation energy, frequency factor in Arrhenius equation, changes of entropy, enthalpy and Gibbs free energy were calculated for the formation of the activated complex from the reagent. The aim of the present microreview is to presented our investigations of the study and characterization of raw rice husks and the obtained from them thermal degradation black and white rice husk ash.

KEYWORDS

Rise husk ash;
Pyrolyzed rise husks;
Structure;
Morphology;
Thermal;
Kinetics characteristics;
Aerosil.

INTRODUCTION

Review of the literature on the problem

A number of reviews[1-6] have been dedicated to rice husks and the products obtained from its thermal degradation at different conditions. Large quantities of rice husks are available as waste from rice milling industry. According to the statistical data of Food and

Agriculture Organization (FAO), the world annual paddy production is approximately 582 million tons. *Oryza sativa L*. husks (Rice husk) comprise 22-25 % of the rice grain and, therefore about 145 million tons of rice husks residue are produced[7]. These husks are not of commercial interest and cause serious pollution problems. It is necessary, then, to consider the use of this residue in polymer formulations with a clear positive effect to the environment. The chemical constituents are found to vary from sample to sample which may be due to the different geographical conditions, type of paddy, climatic variation, soil chemistry and fertilizers used in the paddy growth[4,8-10]. The chemical analysis of these rice husks is found to be for instance 66.67 % carbon, 22.3 % SiO_2, 7.1 % H_2O, 0.82 % Al_2O_3, 0.78 % Fe_2O_3, 1.10 % K_2O, 0.78 % Na_2O, 0.24 % CaO and 0.21 % MgO[2,4]. The organic part is composed approximately of 42.8 % cellulose, 22.5 % lignin, 32.7 % hemicellulose and other organic matter about 2 %. Hemicellulose (xilan) is a mixture of D-xylose-17.52 %, L-arabinose-6.53 %, methylglucoronic acid-6.53 % and D-galactose 2.37 %[2,9]. The nature of silica is mainly amorphous and has been termed *opaline silica*[8]. The silicon atoms are concentrated in the protuberances and hairs on the outer and inner epidermis of the husks in the predominant form of silica gel. Because of its high silica and lignin content, the rice husks are insoluble in water, tough, woody and abrasive in nature with low nutritive properties and resistance to weathering[11]. It is well known that the rice husks have a high calorific value (13 MJ kg^{-1}), high (20-22 %) ash content[5,8,9]. and is sufficient to promote sustainable combustion process, thus reducing the cost of fuel required for the conversion process. Figure 1 shows that milling of 1 tone of paddy produces about 220 kg rice husks, which are equivalent to approximately 150 kWh of potential power.

The energetic balance shows, that utilization of the rice husks as a fuel may be convert paddy milling process from consumer to producer of energy. The obtained ash contains nearly 95 % silica and is an important renewable source of silica. Burning is a cheap method of extracting the silica from rice husks for possible commercial use, but it brings up the associated problems of uncontrolled particle size and variable impurity levels, mainly in the form of intimately mixed carbon. Because of growing environmental concern and the need to conserve energy and resources, efforts have been made to burn the husks under controlled conditions and to utilize the residual ash in a variety of end products. The controlled burning of the raw rice husks (RRH) in air leads to production of white rice husk ash (WRHA) or so-called “white ash” containing almost pure (≥95 %) silica in a hydrated amorphous form, similar to silica gel, with high porosity and reactivity. This silica can be used as an excellent starting materials for synthesis of advanced materials such as silicon tetrachloride[12], magnesium silicide[10], sodium silicate[13], zeolite[14,15] and etc.[16-18]. This silica is an excellent source of very high purity elemental silicon, useful for manufacturing solar cells for photovoltaic power generation and semiconductors[10,19,20]. White rice husk ash can be used also in the cement and fertilizer industries (as a pozzolone and as anti-caking component, respectively)[21-23].

The controlled pyrolysis of the raw rice husks in nitrogen atmosphere leads to production of black rice husk ash (BRHA) or so-called “black ash” which contains different amounts of carbon and silica. This material has very high porosity and may be used as a starting material for the synthesis of silicon carbide[24-26] and silicon nitride[10,27]. Properties like high surface area and porosity give additional advantage to the WRHA and BRHA for their possible use as adsorbents for adsorption of dyes, pigments[3,6] and heavy metal ions[1,5,28] from aqueous solutions, catalytic support and catalyst[29-31].

In the recent years, the raw rice husk and rice husk ash are used as a fillers in rubber[32] and plastic[33-36] composites. The thermoplastic composites, filled with low cost reinforcing natural fillers are widely used in construction and automobile industries and in many

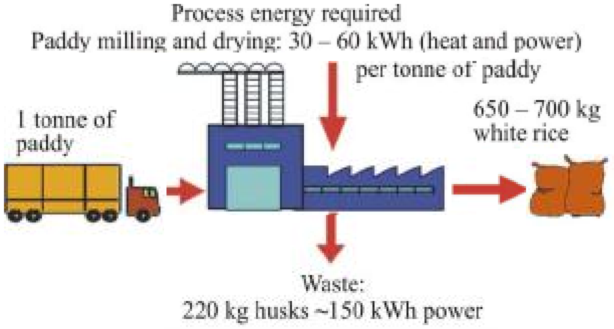


Figure 1 : Power generation potential from rice husk mills

Figure 2 : Laboratory installation for combustion of raw rice husks in fluidized bed reactor: 1-air compressor *Black and Decker*, 2– tank for liquid petroleum gas, 3-distributor for gases, 4-manometer, 5-air Rota meter, 6-quartz fluidized bed reactor, 7-gas burner, 8-asbestos insulator, 9-porous quartz diaphragm, 10-electrical heater, 11-electrical transformer, 12-voltmeter, 13, 14 15-thermo couples, 16-economizer, 17-separator, 18-temperature recorder, 19, 20-thermo regulators, 21-PC

Figure 3: Appearance of ungrounded RRH-a, BRHA-b and WRHA-c

TABLE 1: Bulk and true density of ungrounded and grounded raw rice husks with different moisture

Moisture,	Bulk density, kg m^{-3}		True density, kg m^{-3}	
wt.%	ungrounded	grounded	ungrounded	grounded
7.1	101.2	287.8	1019	1502
24.2	105.5	251.6	1054	1456

consumer goods. The interest towards natural fillers is stipulated by their immanent advantages like availability, high filling levels, low cost, renewability, biodegradability, low density, high specific strength and non-abrasiveness[37-39].

RESULTS

The thermal degradation of the raw rice husks fraction with size 0.63-0.25 mm was carried out in a laboratory installation equipped with quartz fluidized-bed reactor, presented on figure 2.

For the present study, the calculation procedure of Coats and Redfern[40] was used. Data from TG and DTG curves in the decomposition range 0.1-0.9 were used to determinate the kinetic parameters of the process. The kinetic parameters can be derived using a modified Coats and Redfern equation:

Since the pyrolysis of the rice husks is carried out most often in fluidized bed reactors, it is important to know the bulk and true densities of raw rice husks with different moisture and sizes for the assessment of the process hydrodynamics. TABLE 1 shows the data on the bulk and true densities of raw ungrounded and grounded rice husks with different moistures.

As can be seen from TABLE 1, the bulk density of ungrounded rice husks increased with the increase of moisture, whereas the true density decreased. At the same time, the true density of ungrounded husks increased and that of grounded husks decreased. Thus, ground rice husks swell when moist. Density (bulk and true) of ungrounded husk increased with moisture content whereas the density of grounded husk decreased. The same tendency was observed by other authors[16], where it is pointed out that the relationship between the moisture content and true density is linear within the limits of the moisture content in both the ungrounded and grounded conditions of rice husks.

Figure 3 presents the photography of ungrounded raw rice husks and after its thermal treatment in nitrogen or in air atmosphere at 700^0C.

It can be seen from figure 3 that the pyrolysis of rice husk RRH (a) in nitrogen medium gave BRHA (b), while the combustion in air gave-WRHA (c). These products are porous; they have high specific surface area and may be used as adsorbents for different compounds out of solutions. The morphology of raw rice husk, black and white rice husk ash was examined by a scanning electron microscopy. SEM micrographs of raw rice husk, after combustion in air and after pyrolysis in nitrogen atmosphere at 700^0C are presented in figure 4.

The main components of rice husk are in lemma and palea form, which tightly interlock with each other[41]. Figure 4 shows the outer epidermis of raw rice husk, which is well organized and has a corrugate structure. The outer surface of lemma is highly ridged, and the ridged structures have a linear profile. The epi-

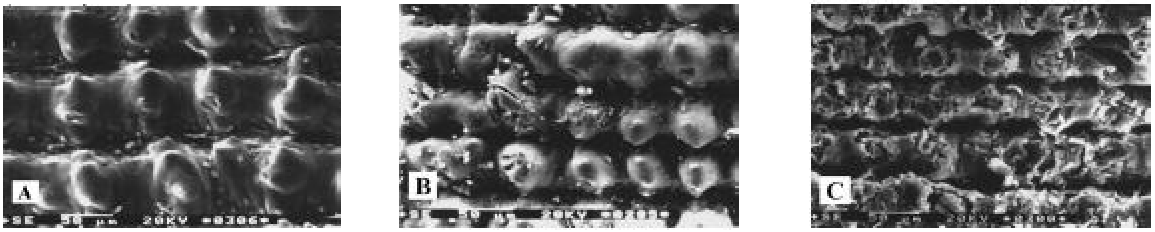


Figure 4 : Scanning electron micrographs of ungrounded RRH (A); WRHA (B); and BRHA (C) at 700°C

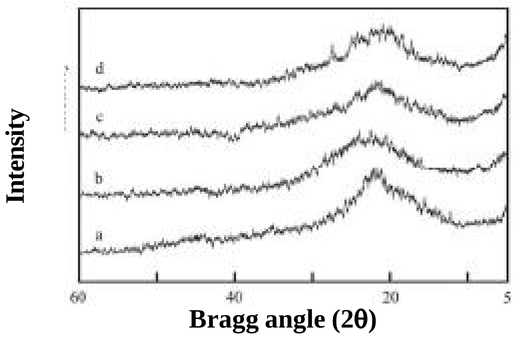


Figure 5: X-ray diffraction patterns of: grounded RRH-a, BRHA-b, WRHA–c and Aerosil A200 Degussa-d

dermal cells of lemma are arranged in linear ridges and furrows, and the ridges are punctuated with prominent globular protrusions[2,11,17,18,41]. The outer surface of lemma also contains papillae and hairs of varying sizes, but they were often broken at their bases in the material examined, and therefore are not illustrated. As can be seen in figure 4A, the structure of raw rice husk was globular. The relatively stable Si-O carcass and biomass assembled around it formed the structure of rice hull. The silicon atoms are presented all over, but are concentrated in the protuberances and hairs (trichomes) on the outer and inner epidermis, adjacent to the rice kernel. After combustion of rice husk in air (Figure 4B), the morphology tended to maintain its original shape although the product is brittle and loose when carefully pinched with the fingers. The only difference that can be observed was that the globules were shrinked and compacted due to the release of the volatile products. The hard residue was formed of almost pure SiO_2 (96.8 %). As it has been pointed out[17], the rate of combustion process depends strongly on the vapor diffusion rate from the bulk of the spherical globules. The structure of the pyrolysis product obtained in nitrogen medium was also globular (Figure 4C), but due to the lower percentage of volatile products released, the solid residue contained significantly more carbon (22.6 %). In this case, therefore, the initial globular structure of rice husk was also preserved due to the high thermal stability of SiO_2. The last two SEM micrographs showed that many residual pores are distributed within the ash samples, indicating that WRHA and BRHA is highly porous material with large internal specific surface area. The rice husk might have become broken up during thermal decomposition of organic matter, thus obtaining highly porous structure. By comparison of these micrographs, it is observed that the surface of raw rice husk is relatively nonporous, whereas burned or pyrolyzed rice husk exhibit porous surface, as indicated by the pore structure analysis (nitrogen adsorption).

The pyrolysis of rice husk caused decomposition of organic part and breaking of the bonds with Si. The XRD patterns of the raw rice husks, pyrolyzed and combusted rice husks, as well as Aerosil A200 (Degussa AG, Germany) which is non-porous highly dispersed silica are shown on figure 5 for comparison[42].

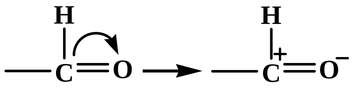
Figure 5 shows X-ray diffraction analysis on the rice husk before and after thermal decomposition in nitrogen or air medium. All the tree samples were amorphous, although a broad diffused peak centered at about $2\theta = 22.5°$ was observed. No reflexes, characterizing cristobalite or tridymite phase were noticed in the samples studied, indicating the absence of any crystalline phases. Curve (a) from figure 5 represents the X-ray diffraction of the raw rice husk. A broad hump around $2\theta = 22°$ was noticed, indicating the presence of amorphous silica (disordered cristobalite). The same results were obtained for the BRHA and WRHA, as well as for Aerosil Degussa (curve c) used for comparison. The maxima of the diffused peaks were found to vary from $2\theta = 22°$ for raw rice husks to $2\theta= 20.7°$ for white ash. The pyrolyzed rice husks showed an almost flat maximum spreading from $2\theta = 21°$ to $2\theta = 26°$. This could be attributed to a gradual change in the bonding of silicon with organic material in raw rice husks

TABLE 2: Physicochemical characteristics of the RRH, WRHA, BRHA and AR

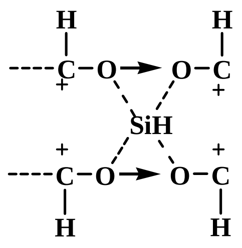
Parameter	RRH	WRHA	BRHA	AR
SiO_2, mass %	20.2	94.2	54.0	100
Moisture, mass %	7.1	–	–	–
Mean particle size, μm	80	50	60	20
Surface area, $m^2\ g^{-1}$	<1	228	141	273
True density, $g\ cm^{-3}$	1.47	2.2	1.8	2.2

to silica-silica bonding in white ash. According to[4,18,42,43] the partially crystalline cellulose in naturally aged raw rice husks show an XRD peak at 2θ = 26.7°. The XRD pattern for the raw rice husks, presented on figure 5 with its maximum at 2θ = 23° suggests that the silicon in raw rice husk is bonded with organic material.

Going a little deeper into the structure of the organic compounds present in rice husks, the concept of the bonding of silicon with organic molecules can be confirmed. About the bonding of silicon with organic molecules, it may be said that cellulose $(C_6H_{10}O_5)_n$, being a polysaccharide and the main component of rice husk, does not seem to possess considerable bonding ability. Lignin, which coexists with cellulose, is mostly inert and therefore it is also not expected to be suitable for bonding. The remaining four organic components included in hemicellulose are aldehydes (monosaccharides), which become polar due to an electrometric effect. In the aldehyde group, the electrometric effect operates as shown bellow[17]:



This type of electron transfer is brought into play only under the influence of an attacking reagent. The nature of silicon bonding in rice husk is complex and it appears to be bonded with the carbohydrates only. The possible bonding of silicon with four aldehyde residues in the raw rice husk, as indicated above, may be illustrated with the following scheme[17,44]:



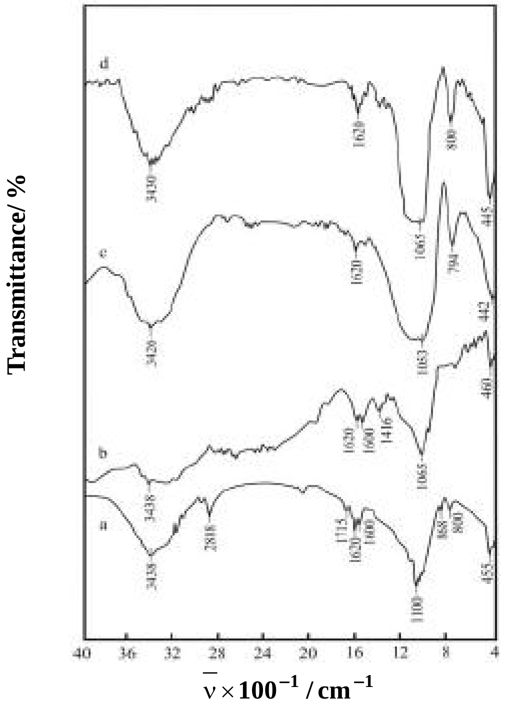


Figure 6: IR spectra of RRH-a; BRHA-b, WRHA-c, and Aerosil A200 Degussa-d

The pyrolysis of raw rice husk causes the decomposition of the organic material and breaking of the bonds between silicon and the organic material. The Si-O groups become attached to each other to produce a low form of cristobalite. The resulting carbon and amorphous silica in the white ash showed an XRD pattern with a broad maximum. Upon complete burning, the single phase amorphous silica shows a diffused XRD peak with a maximum at about 2θ = 21.8°. Thus, the X-ray diffraction patterns of rice husk ash showed a curve resembling that of silica gel without any characteristic peak. For both thermally treated samples, peaks characterizing cristobalite and tridymite phases were not registered. Cristobalite was detected at temperature above 727^{0}C, while at 1150^{0}C both cristobalite and tridymite were present. These results are in consistence with those obtained in other studies[45]. Aerosil Degussa used as reference has also amorphous structure similar to that of WRHA.

According to the data from X-ray analysis (Figure 5) the all used products are amorphous. The physicochemical characteristics of these are shown in TABLE 2.

The different groups in which silicon exists, e.g. siloxane Si–O–Si and silanol Si–OH, are best observed

TABLE 3: Absorption bands in the IR spectra and their assignment

Region, cm^{-1}	Assigned to	Refs.
3600–3100	O–H stretching vibration	[9-11], [25,46]
3000–2850	C–H stretching vibration	[9,11,25]
1720–1700	C–O stretching vibration of ketones, aldehydes, lactones or carboxyl groups	[9,11,47]
1620	H_2O bending vibration	[10,11,46,47]
1615–1600	Aromatic C=C vibrations, activated by neighboring oxygen groups	[9,25]
1500–1415	C–H deformation	[25]
1500–1200	CH_2, CH_3, $Si(CH_3)$, $C(CH_3)$	[25]
1500–1000	Aromatic C=C skeletal vibration	[25]
1360–1310	C–C and C–O skeletal vibration	[11,25]
1100–1000	Si–O stretching vibration	[10,11,25,43,46]
970	SiC (reflection)	[25]
898–825	Characteristic Si–C bonds appears beside Si–O vibrations	[25,46]
825–800	Antisymmetric Si–O stretching vibration	[25,43]
796, 1093	Characteristic of Si–O bonds	[10]
480–445	Bending vibration of O–Si–O	[10,11,25,43]

in IR spectra. Figure 6 presents IR absorption spectra of raw rice husks after pyrolysis in nitrogen or combustion in air at 700^0C and for comparison-Aerosil Degussa.

Infrared spectroscopy provides information on the chemical structure and surface functional groups of the samples. The IR spectra of rice husk gave typical bonds of Si–O–Si stretching (very strong at 1096 cm^{-1} and strong at 798 cm^{-1}) and bending vibrations (very strong at 466 cm^{-1}). The bands at 3437 and 1633 cm^{-1} correspond to the O–H vibrations[9-11,25,42,43,46,47]. It can be seen from figure 6 (spectrum a) that raw rice husks are characterized by broad band between 3750 and 2800 cm^{-1}. The O–H stretching mode of hexagonal groups and adsorbed water can be assigned to this band. The position and asymmetry of this band at lower wave numbers indicate the presence of strong hydrogen bonds. A very weak band at 3750 cm^{-1} can be assigned to isolated O–H groups. The adsorption band observed at 2920 cm^{-1} was related to aliphatic C–H groups and the very small peak near 1720 cm^{-1} was attributed to the C=O stretching vibrations of ketons, aldehydes, lactones or carboxyl groups. The weak bands at 1600 cm^{-1} and 1500 cm^{-1} correspond to bending vibration of H_2O molecules physically adsorbed onto rice husks and C–H deformation vibrations, respectively. The weak band at 1400 cm^{-1} corresponds to a C–O stretching vibration of carboxylate groups. The predominant absorbance peak at 1320 cm^{-1} was due to stretching vibrations and the one at 450 cm^{-1} was due to bending vibration of siloxane bonds (Si–O–Si). The peaks between 1200 and 700 cm^{-1} are attributed to vibration modes of the Si–O network.

After the pyrolysis of rice husk in nitrogen medium, the IR spectrum of the black ash obtained did not differ significantly from that of raw rice husks, except for the quite higher intensities of the bands at 1045 and 450 cm^{-1}. This can be explained with the decrease of organic matter content and its transformation into active carbon. The thermal treatment of rice husk in air, however, resulted in very different IR spectrum (Figure 6, spectrum c). Wide, highly intense peak was observed with maximum at 3420 cm^{-1}, attributed to the stretching vibrations of silanol groups. The bands at 1050-1150 and 790 cm^{-1} correspond to the Si–O stretching vibration and the bending vibration at 450 cm^{-1} appeared sharper as the organic matter was no longer present. The positions of this feature are the same as those observed for commercial grade silica. Probably, the silicon atom was initially attached to the oxygen atom in raw rice husk and, after the thermal decomposition, the combination of silicon and oxygen atoms lead to the formation of amorphous silica. In addition, it can be also observed that the peak for the white ash sample was sharper peak than that of the black ash sample, indicating that the percentage of silica contents increased when the rice husk is burnt in air. The IR spectrum of white rice husk ash silica is the same as those of Aerosil A200 Degussa. This means that both products have a similar nature. In TABLE 3 are summarized the absorption bands and their assignments observed in the IR spectra of the initial and thermally treated rice husks.

According to the data obtained from the thermogravimetric analysis, the thermal decomposition of rice husks in air medium occurred in three main stages of mass loss, namely, removal of moisture (drying); release of organic volatile matters (devolatilization) and

TABLE 4: Kinetic characteristics of rice husk thermal degradation

Parameter	Sample					
	A		B		C	
	$T < T_p$	$T > T_p$	$T < T_p$	$T > T_p$	$T < T_p$	$T > T_p$
$T_{p\ (exp.)}$, K	593		633		853	
$T_{p\ (calc.)}$, K	597		634		855	
E_A, kJ mol^{-1}	187.1	23.1	175.1	5.3	228.3	54.8
A, min^{-1}	3.45×10^{14}	2.04×10^{-1}	1.78×10^{13}	5.60×10^{-3}	6.49×10^{11}	3.89
k, min^{-1}	1.14×10^{-24}	1.85×10^{-3}	6.32×10^{-2}	2.05×10^{-3}	6.78×10^{-3}	1.17×10^{-3}
$-\Delta S^{\neq}$, J mol^{-1}K^{-1}	14.7	306.4	39.9	336.6	69.9	284.5
P	0.171	9.88×10^{-17}	8.3×10^{-3}	2.60×10^{-18}	2.2×10^{-4}	1.38×10^{-15}
$\Delta H^{\neq}$, kJ mol^{-1}	182.2	18.2	169.8	0.04	221.2	47.7
$\Delta G^{\neq}$, kJ mol^{-1}	190.9	199.9	195.1	213.1	280.8	290.4
R^2	0.9899	0.9951	0.9988	0.9822	0.9852	0.9947

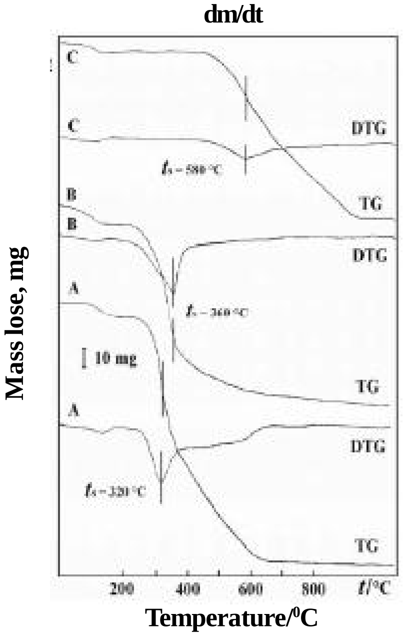


Figure 7: TG and DTG curves of the samples: combustion in air flow of grounded rice husks (A), pyrolysis in nitrogen flow (B), and burning in air flow of carbonized rice husks (C)

oxidation of fixed carbon (slow combustion)[4,42,44,48]. The TG and DTG curves of studied samples are presented on figure 7.

As can be seen from figure 7 (curve A), the mass loss in the first stage took place in the range 77–150^{0}C and is accompanied with small endothermal effect. The mass loss is about 7 % and it is associated with the evolution of adsorbed water in the sample and external water bonded by surface tension. The observed features of the thermal decomposition of rice husks can be explained on the basis of the decomposition behaviors of its major constituents: cellulose, hemicellulose, lignin and ash. According to Stefani et al.[7] hemicellulose is degraded first at temperatures between 150 and 350°C, cellulose from 275 to 380^{0}C and finally lignin from 350 to 550^{0}C. The second and major mass loss of nearly 50 % is attributed to the breakdown of the cellulose constituent to combustible volatiles, water, carbon dioxide and char. Using a pyknometer as described previously, the true densities of the white and black rice husk ash were measured to be 2200 and 1800 kg m^{-3}, respectively. It is considerably more than the true density of grounded row rice husk. The lower density of the latter was due to the high content of active carbon in it (≥ 20%).

The kinetic mechanism and kinetic parameters of non-isothermal degradation of rice husks in nitrogen or air medium have been described in detail in[49]. The smaller kinetic parameters obtained in the third stage, compared to these obtained in second stage, may be due to the fact that lignin, which has lower decomposition rates than cellulose and hemicellulose components in rice husk, was condensed to char.

The TG data were evaluated using 14 mechanism-based equations. The best correlation was obtained with the equation of Ginstling-Brounshtein[50,51].

As can be seen, the kinetic curves have two linear regions: the first one at temperatures lower than $Ò_{ð}$ (peak temperature in DTG curve) is steeper and the second one at higher temperatures has a smaller slop. For detailed study of the mechanisms of both stages, the values of the activation energy E, frequency factor A, change of entropy $\Delta S^{\neq}$, enthalpy $\Delta H^{\neq}$, Gibbs free energy $\Delta G^{\neq}$ were calculated for the formation of the active complex from the reagent and $P = \exp(\Delta S^{\neq}/R)$ is the steric factor (TABLE 4).

Beside the value of the correlation coefficient of the linear regression analysis R^2, the second criterion used was $T_{p(calc)}$. This temperature was calculated from the cross point between the corresponding straight lines and was compared to the experimentally determined reference temperature $T_{p(exp)}$ which, in turn, corresponds to the peak temperature in the DTG curve. As can be seen from the table, the difference between these two temperatures was less than 4^0C. It means that the equation of Ginstling-Brounshtein was selected correctly and that a study on the kinetics of pyrolysis of rice husk should take into account the diffusion of volatile products from inside layers of the biomass. The higher values of E observed at $T< T_p$ show that the initial release of volatile products occurs under kinetic-diffusion control while the much lower values of E at $T< T_p$ indicate that pyrolysis takes place under typical diffusion control. The similar values of activation energy found for the first stages samples A and B show that the release of volatile products during burning in air or pyrolysis in nitrogen medium occurs by similar mechanisms. The difference in E values for second stage shows that the release of volatile products in nitrogen occurs at lower activation energy due to their lower content in the samples. At the same time, the oxidative burning of the pyrolysis product (sample C) occurred at much higher activation energies for both stages. This means that the diffusion of the volatile products was much more difficult in sample C because of the hardly deformable Si-O carcass. For monomolecular reactions of decomposition taking place within the solid phase, values of the frequency factor of the order of 10^{14} show that the rotations of the active complex and the reagent do not change during the reaction. At values of ca. 10^{11} the reagent can rotate freely while the active complex can not rotate**[52]**. The negative values of the change of entropy of the formation of the active complex mean that the active complex can be characterized by a much higher "degree of arrangement"**[53]**. Besides, higher degree of "arrangement" was observed in the second stage (higher value of $\Delta S^{\neq}$). The significantly lower than unity values of the steric factor P in the second stage give enough grounds to classify this stage as "slow"**[53]**. For the first stage, however, the values of P are much closer to unity, so the first stage may be considered as "faster"**[54]**.

CONCLUSION

The method of thermal treatment of raw rice husks helps to solve the disposal and pollution problems of the rice milling industry and give an excellent starting materials for preparation of advanced high-quality ceramic powders, such as silicon carbide, silicon nitride and magnesium silicide, which are good for application in high temperature material engineering, especially for turbine engines. In addition, small scale of pure silica powder can be widely used for production of high purity elemental silicon for electronic, adsorbents, catalyst support, as tixotropic agents, thermal insulator and filler of rubbers and plastics, etc.

The results obtained were considered enough to conclude that the cheap raw rice husks and the products of its thermal degradation (BRHA and WRHA), after vigorously grounding and mixing, can successfully be used as fillers for polypropylene to replace the expensive synthetic additive Aerosil in the preparation of different composites.

Currently the using of the raw rice husks and the products of its thermal degradation is an object of intensively studies. The abundance of a waste from paddy milling industry, as well as its interesting complex of behaviors are prerequisite for success for obtaining of cheap and valuable products and gives a new alternatives for its applications.

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