

## Changes in structure of solid pyrolysis residue during slow pyrolysis of rice husk

S. Uzunova<sup>1</sup>, D. Angelova<sup>1</sup>, B. Anchev<sup>1</sup>, I. Uzunov<sup>2\*</sup>, A. Gigova<sup>3</sup>

<sup>1</sup> University of Chemical Technology and Metallurgy Sofia, 8 St.Kl.Ohridski Blvd., 1756 Sofia, Bulgaria

<sup>2</sup> Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G.Bonchev Str., bl.11, 1113 Sofia, Bulgaria

<sup>3</sup> Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, Acad. G.Bonchev Str., bl.10, 1113 Sofia, Bulgaria

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The research provides the basis for development of a new environmental material with controllable characteristics, suitable for producing of value-added carbon/silica containing materials. The subject of the study is to determine the influence of the pyrolysis temperature on the specific surface area and porosity of charcoal obtained by slow pyrolysis in the temperature range 250-700°C of acid leached rice husks.

The char's structure was set out by the mercury porosimetry and Brunauer-Emmett-Teller method. The phase composition of the solid residue after pyrolysis and carbon/silica ratio therein has been determined by thermal analysis (TG/DTA/MS) and XRD. The morphology of the materials has been studied using scanning electron microscopy.

It was established that the slow pyrolysis in the investigated temperature range results in a solid residue with predominantly macro-porous structure and pore size distribution between 50 and 200 µm. The sample obtained at 480°C is characterized by the largest total pore volume and the largest average pore diameter. With increasing the pyrolysis temperature C:SiO<sub>2</sub> ratio in the solid pyrolysis residue decreased from 1.38 to 0.85 and specific surface area increased from 7.0 up to 440.0 m<sup>2</sup> g<sup>-1</sup>.

**Keywords:** rice husk; pyrolysis; porosity; specific surface area; morphology

### 1. INTRODUCTION

In recent years, in relation with the periodical energy crises and the depletion of raw material stocks, particular attention is paid to obtaining energy and value-added products from renewable agricultural wastes. The rice husks, a by-product of the rice milling industry are produced in large quantities as a waste. The limited applicability of the rice husks as foodstuff for cattle is creating an ecological problem, connected with the storage and management of huge amounts of waste. On the other hand the specific phase composition, structure and properties of the husks renders them suitable for preparing different C/SiO<sub>2</sub> containing materials [1,2]. The rice husks possess, although a low, caloric effect. So they can be considered also as a renewable power source [3]. In recent years are offered different methods associated with the conversion of rice husks into the high-tech products [4-6].

Between the thermo-chemical conversion methods for processing of biomasses most often used pyrolysis. The process is related to obtaining a liquid phase, char and gaseous fractions (fuel gases). There are two approaches for the conversion

technology. So called conventional pyrolysis, is to maximum the yield of pyrolysis oil and/or fuel gas. The conditions are high temperature and high heating rate. The second enhanced the char production at the low temperature and low heating rate. One of the possible applications of solid pyrolysis residue is use it directly or after activation as biosorbents [5,7]. They are biodegradable and have high adsorption properties resulted from their morphology and surface functionalities [8]. There is no need to regenerate them because of the low production cost [5,9,10]. Their application is a good practice and has received much attention in sorption of various organic or inorganic pollutants from aqueous medium [11,12].

The use of the solid pyrolysis residue as adsorbent is related to obtaining of a material with suitable porous structure, high specific surface area and surface functionalities which providing a high adsorption capacity and selectivity [13,14]. Ways to get the carbon containing adsorbents with a developed porous structure are the use of suitable activating agents and/or controlling the pyrolysis conditions [15-17].

There have been several reports on the pyrolysis of rice husks which deal with the relation between the pyrolysis conditions with char structure. The development of advanced fast pyrolysis processes for bio-oil production has gained much attention

\* To whom all correspondence should be sent:  
E-mail: [uzunov\\_iv@svr.igic.bas.bg](mailto:uzunov_iv@svr.igic.bas.bg)

recently, because they offer a convenient way to convert agriculture wastes into biofuels and carbonaceous value-added products. That is why the studies are related to determination the impact of the temperature, heating rate and pressure on the quantity, phase composition and morphology of final products in fast pyrolysis. Hu et al. [18] determined the pyrolysis reactivity's of rice husk char and the evolution characteristics of char structure during rapid pyrolysis. Liou [19] investigated the effect of heating rates on the morphology and chemistry of the products from carbonization of rice husks. Kumagai et al. [20] and Bharadwaj et al. [21] also published data which dealt with the relationship between the fast pyrolysis conditions and char structure. The general conclusion is that the fast pyrolysis is associated with obtaining a small amount of solid pyrolysis residue with predominantly microporosity and narrow pore size distribution. These can be explained by the very fast decomposition of lignin-cellulose matter and evolution of volatiles during rapid pyrolysis, thus leaving a highly microporous structure.

It is reasonable to expect that the slow pyrolysis will lead to other, different phase and structural changes in solid pyrolysis residue.

In this study, the slow pyrolysis which provides a high yield of solid residue was used in a fixed bed induction heated reactor. In particular, the impact of pyrolysis temperature at a constant heating rate and retention time on the pore structure of rice husks char was investigated. The effect of the pyrolysis temperature on the carbon:SiO<sub>2</sub> ratio in solid pyrolysis residue was also discussed.

The results indicated that the slow pyrolysis temperature had an essential impact on the char's structure. The resulting solid pyrolysis products are characterized by a varied in size porous structure. The same is formed predominantly by meso- and macro pores with a wide range of pore size distribution. This fact is important when the solid residue from thermo-cracking of rice husks will be used as adsorbent [22-24].

## 2. EXPERIMENTAL

### 2.1 Materials

Rice husks (RH) were obtained by rice threshing performed in 2010 from Pazardjik region, Bulgaria. The husks with prevailing particle size above 5 mm were initially washed several times with water to remove any mechanical impurities. Determined amount of ash in the raw rice husks is 21 wt.%. Except the main quantity of amorphous silica, the

ash contains some other inorganic admixtures listed in Table 1. To reduce the content of these admixtures RH were treated with 12 N HCl, at hydro-module 3:1, for 3 hours at the boiling temperature of the acid. A reflux condenser was used. The acidified sample was washed with deionized water until pH 6.5 was reached and dried at 110° C to a moisture content less than 5 wt.%.

### 2.2 Pyrolysis

A weighted amount of the so pretreated husks were pyrolysed in a temperature interval 250-700° C. The following series of samples, designated as *B1* (250°C), *B2* (350°C), *B3*

(480°C) and *B4* (700°C) were obtained. The fixed bed slow pyrolysis experiments were performed in a vertical tube stainless steel electrically heated reactor, equipped with temperature controllers, under a residual pressure of 1.33 Pa. The reactor comprised a 240 mm (L) x 40 mm (ID) with 170 mm long heated zone. The liquid products were collected in a trap between the reactor and vacuum pump, maintained at the temperature of 2-3° C. The temperature in the reactor was increased linearly from room temperature up to the value needed for pyrolysis with a heating rate of 4° min<sup>-1</sup> and temperature retention for 4 hours. The time within which the temperature is maintained constant, is defined as "retention time". The sample was taken out after cooling the system down to room temperature, at atmospheric pressure. The yields of the solid pyrolysis residue were calculated based on the mass of raw rice husks fed.

### 2.3 Samples characterizations

The carbon/SiO<sub>2</sub> weight ratio in the solid pyrolysis residues has been determined applying thermal analysis (TG/DTA) accomplished with a SETARAM *LabsysEvo* device, in a corundum crucible, at a heating rate of 10° min<sup>-1</sup> in air. A mass spectrometer detector coupled to the device was used for the evolving gas analysis. The signals for mass numbers of 18 and 44 were continuously detected.

The phase composition of the samples has been carried out on the basis of the data, recorded by a diffractometer Philips ADP 15 with Cu K<sub>α</sub> radiation.

Area of the pores as well as the bulk density was determined by mercury intrusion porosimetry on a MICROMERITICS Auto-Pore 9200 apparatus. Volume intrusion curves were obtained for every sample from 0.01 up to 34.84 MPa pressure, which

corresponded to a pore diameter range from 262.7  $\mu\text{m}$  to 0.042  $\mu\text{m}$ . Prior to

porosimetry analysis the samples were dried at 110° C for 48 h. The specific surface area was assessed by BET nitrogen adsorption measured in a static volumetric device Area Meter, Strolein.

The morphology of the surface of the raw rice husks and pyrolyzed ones was observed with SEM using JEOL- Superprobe 733 microscope, applying the appropriate magnification.

The total ash content into the raw RH was analyzed gravimetrically. The inorganic admixtures were determined by flame atomic absorption analysis (AAA) by spectrometer Solar M.

### 3. RESULTS AND DISCUSSION

#### 3.1 Phase composition and morphology

The data of the inorganic admixture amount in the raw RH before and after treatment with hydrochloric acid evaluated by AAA are presented in Table 1.

**Table 1.** Inorganic admixture amount in the raw RH before and after acid treatment.

Element	Amount, wt. %
Carbon	38.4
Hydrogen	4.3
Oxygen	36.08

The low content of inorganic admixtures in the ash residue of leaching rice husks is reason hereafter to talk about phase of silica in solid pyrolysis residue.

The elemental microanalysis was used to investigate the carbon/silica weight ratio in the acid treated raw rice husks, Table 2. According to the results obtained the carbon/silica weight ratio in the acid leached raw rice husks amounted to 1.81 weight percent.

**Table 2.** Elemental composition of acid leached raw RH.

Element	In raw RH, $\mu\text{g g}^{-1}$	After leaching, $\mu\text{g g}^{-1}$
K	580	62
Na	370	60
Fe	330	38
Ca	103	*BDL
Cu	12	BDL
Mn	10	BDL
Zn	7	BDL
Mg	5	BDL

\*BDL, below detection limit.

On the basis of the thermogravimetric analysis data, Fig. 1 (a) the weight C:SiO<sub>2</sub> ratio in the samples B1-B4 has been determined. The effect of pyrolysis temperature on the yield and carbon/silica ratio of the chars is shown in Table 3.

**Table 3.** Yield of the carbon-containing residue and C:SiO<sub>2</sub> weight ratio as a function of the pyrolysis temperature.

Sample	T <sub>pyrolysis</sub> , °C	Yield, wt. %	Ratio C:SiO <sub>2</sub>
B1	250	58	1.38
B2	350	52	1.08
B3	480	49	0.96
B4	700	46	0.85

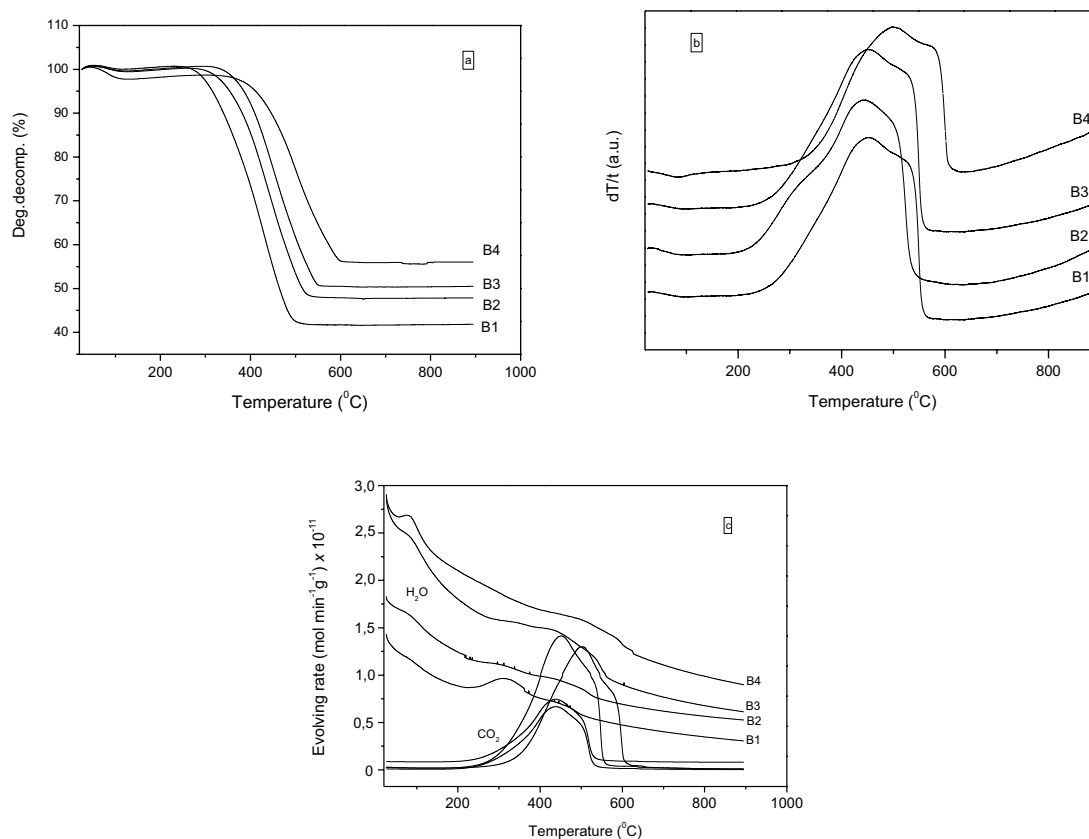
Actually the char represents a mixture of some quantity undecomposed residues of the lignin-cellulose material, highly carbonized rice husks and silica. The change of the C/SiO<sub>2</sub> ratio shows that with increasing of pyrolysis temperature the solid pyrolysis residue become increasingly less carbonaceous in nature and vice versa for the silica.

The thermal effects (DTA) and gas formation rates under conditions of linear temperature increase, in air medium for samples B1-B4 are presented on Figures 1(b) and (c).

The rice husks as a lignocelluloses' material is composed of various type biopolymers containing cellulose, hemicellulose, lignin and amorphous SiO<sub>2</sub> [4]. The chemical nature of biogenic silica in rice husks has discussed by a number of authors [25,26]. Upon pyrolysis condition in rice husks start some destruction processes. Hemicellulose started its decomposition easily; cellulose pyrolysis takes place at a higher temperature range while the lignin decomposes at a slow rate in the entire operating temperature interval [24]. The degradation reactions include depolymerization, dehydration, decarboxilation and oxidation of the lignocelluloses' matrix.

For example: sample B1, obtained at 250° C, contains in itself not completely decomposed residuals of cellulose and lignin. The exothermal effect in the interval 210 - 370° C is associated with the destruction of the remaining quantity of cellulose, contained in this sample. The process is accompanied by the evolving of the main quantity of water and a small amount of CO<sub>2</sub>, as a consequence of the decomposition of the nuclei of the cellulose chain. The second exothermal effect with a maximum at 440° C corresponds to the full destruction of the lignin residuals and oxidation of the char, completed at 540° C. As a result of the decomposition of the condensed nuclei of the lignin mainly CO<sub>2</sub> is liberated.

The results from TA/MS analysis of samples B2-B4 confirmed the presence of undecomposed part of the lignin-cellulose material in the solid pyrolysis residue. According to the data of the TG analysis, the moisture content in carbonized rice husks amounted to 5 wt. %.

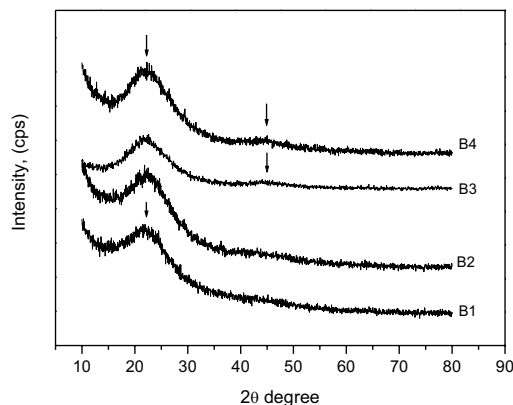


**Fig.1.** TG curves (a); DTA curves (b); gas formation rates and products distribution (c) during the thermal analysis of the samples in air atmosphere

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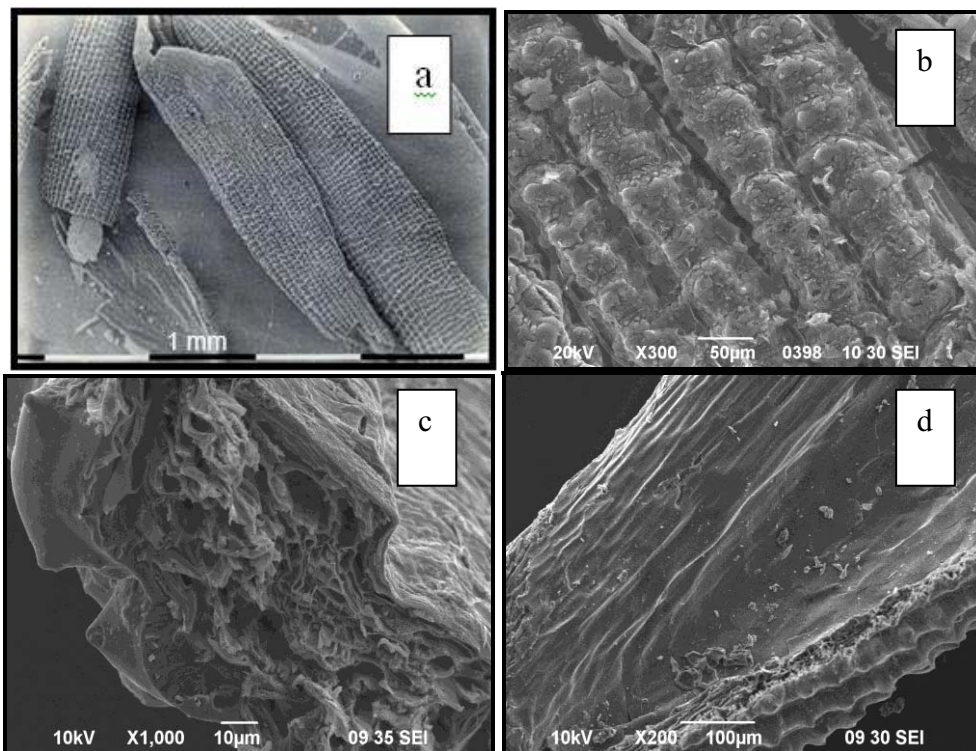
The X-ray diffraction patterns of the samples are presented in Fig. 2. The possible bonding of silicon with monosaccharides in rice husks has already been represented by Patel et al. [27]. The pyrolysis causes a decomposition of the organic material and breaking of the bonds between silicon and the organic matrix. The Si-O groups become attached to one another to produce a low form of cristobalite and tridimite. The resulting material, containing a mixture of amorphous silica and carbon show an XRD pattern with a broad maximum. The results also corroborate the formation of a porous network in the samples. The halo observed at about  $2\theta$  22° corresponds to the presence of amorphous SiO<sub>2</sub> [28], but also shows the typical turbostratic structure with interlayer distances of graphenes substantially higher than those in graphite. The halo at  $2\theta$  44° is typical for carbonized cellulose and reflects the initial formation of (100) planes, related to the graphite structure [29]. It becomes more

pronounced with increasing the temperature of pyrolysis.



**Fig.2.** XRD patterns of the pyrolyzed RH

The cellulose and hemicellulose under conditions of pyrolysis degrade under cyclization and dehydration followed by transglycosylation. The mechanism of decomposition of lignin also occurs *via* dehydration [30]. The process is accompanied by intensive liberation of gases and liquid phase, containing different hydrocarbon compounds, CO, CO<sub>2</sub> and H<sub>2</sub>O. The rapid mass transfer from the inside of the

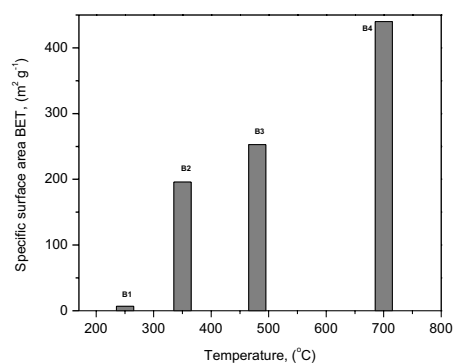


**Fig.3.** Micrographs of raw RH (a), outer epidermis (b), cross-section (c) and inner epidermis (d) of rice husks carbonized at 480° C.

particles to the surface caused structural evolution and morphological changes of the solid residue. Some part of fluids is being deposited on the char surface, determining its surface functionalities. Change in the morphology of rice husks in the pyrolysis process, studied by means of scanning electron microscopy, is demonstrated in Fig. 3.

A typical structure with granular formations located linearly on the outer epidermis as well as the fibrous structure of the inner epidermis can be seen in Fig. 3(a). It was established that the silica is concentrated predominantly in the outer surface and in a less amount in the inner surface of the RH [31]. After carbonization the rice husks appear to be cracked, Fig. 3(b). The size of small grains on the outer epidermis is reduced. Nevertheless the corrugated structure of the outer epidermis was kept in the solid pyrolysis residue. This means that after carbonization the solid pyrolysis residue retains skeleton of lignocelluloses' matrix, building the cell walls in which remains dispersed amorphous silica. After pyrolysis the lamellar inner epidermis remains undestroyed, Fig. 3(d). Evaporation of volatile matters creates in interior structure of the pyrolyzed RH many pores of different size with rough surface and irregular outlet, Fig. 3(c).

The increase of the pyrolysis temperature leads also to a change in the specific surface area of the obtained materials, varying in a range from 7 up to 440 square meters per gram, Fig. 4.



**Fig.4.** Dependence between BET specific surface area of the samples and the pyrolysis temperature.

### 3.2 The pore size distribution

The pore size distribution is a function of the pyrolysis temperature and phase composition of the lignocelluloses precursor. This is the most important dimension for characterizing the structural heterogeneity of the solid residue and is closely related to kinetic properties of porous materials [20].

The porosity characteristics of the samples, determined by mercury porosimetry are depicted in Table 4. The experimentally obtained data demonstrate that the porosity, respectively the total volume of the pores of samples B1, B2 and B4 have

similar values while the values for sample B3 are higher with about 9%. The sample B3 is characterized also by the greatest average pore diameter and the lowest bulk density.

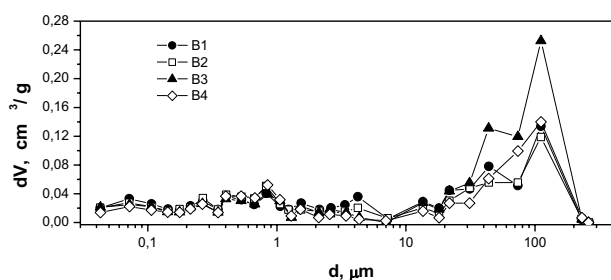
**Table 4.** Porosity characteristics of the samples determined by mercury porosimetry.

Characteristics	B1	B2	B3	B4
Total pore volume, cm <sup>3</sup> g <sup>-1</sup>	0.898	0.814	1.053	0.778
Porosity, %	52.38	52.04	57.09	52.95
Total pore area, m <sup>2</sup> g <sup>-1</sup>	6.652	6.369	5.869	5.164
Average pore diameter, μm	0.540	0.511	0.718	0.603
Bulk density, g cm <sup>-3</sup>	0.583	0.640	0.542	0.680

The differential curves of the pore volume distribution with respect to diameter for the B1-B4 samples are exhibited in Fig. 5. All the porosity diagrams have a similar appearance, which shows that the analyzed samples possess pores with sizes varying within a wide range of values. The main share of all the pores belongs to the pores with large volumes and diameters within the interval 50-200 μm.

The maximum peak in the differential distribution curves for all four samples corresponds to the percentage of the total pore volume, as follows:

- For B1 - 14.9 %;
- For B2 - 14.6 %
- For B3 - 24.0 % and
- For B4 - 18.0 %.



**Fig.5.** Pore volume distribution by pore diameter for samples B1-B4.

The results demonstrate that the prepared carbonized rice husks possess multi macroporous structure. The presence of the such structure, as a rule ensures high sorption ability of the material [32].

The theory of mercury porosimetry conditionally accepts that the diameter, determined by the integral dependence with respect to the pore volume and pore surface area at which there starts a steep increase is the value, dividing the pores in two kinds: “micro” pores, with pores diameter less than the value of the inflection point and “macro” pores, Fig. 6.

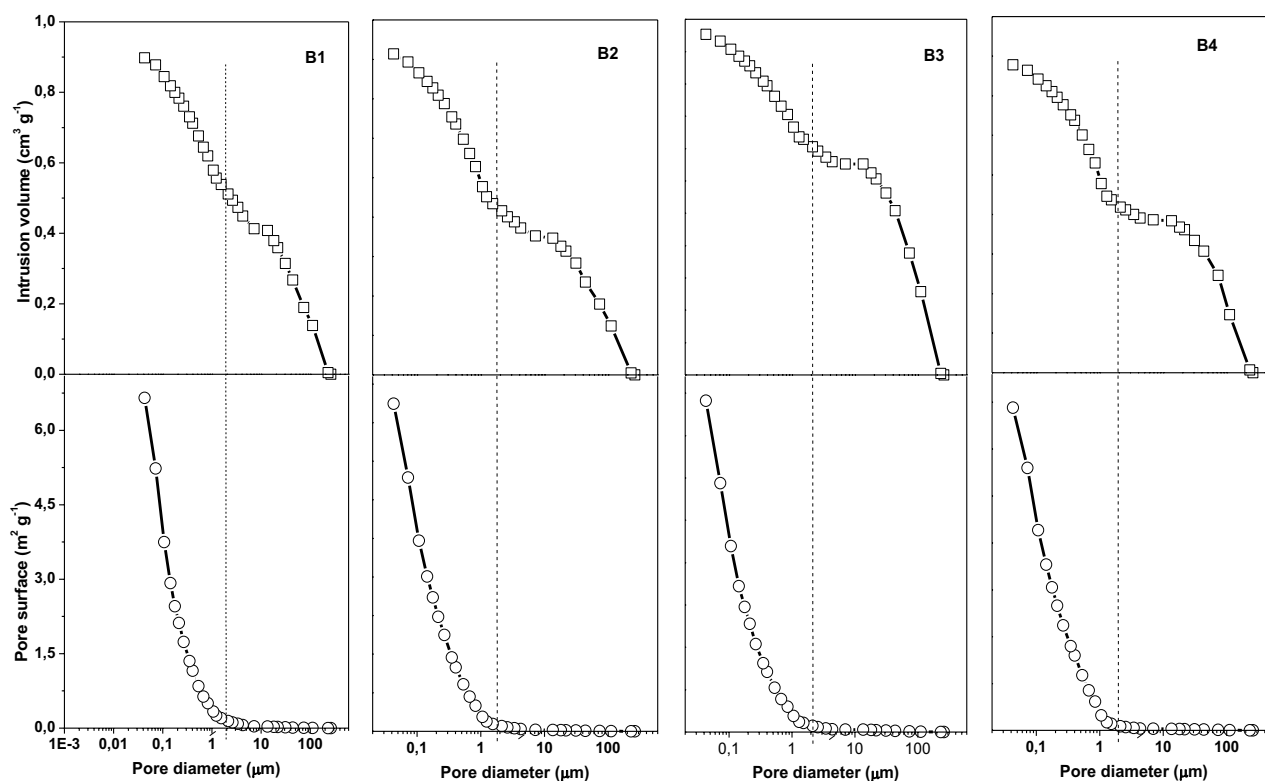
It should be noted that in according to IUPAC the classification of the pores as micro-, meso- and macropores is subject to certain requirements for the pore-width [33].

Table 5 represents the conditional dividing of pores in view of their size in the prepared samples.

**Table 5.** Provisionally pore size distribution in the pyrolyzed rice husks.

Characteristics	B1	B2	B3	B4
Value of the inflection point, μm	1.88	1.76	2.13	1.93
Volume of “micro” pores, cm <sup>3</sup> g <sup>-1</sup>	0.3676	0.3731	0.3424	0.3530
Percent of “micro” pores, %	40.9	45.9	32.5	45.4
Volume of “macro” pores, cm <sup>3</sup> g <sup>-1</sup>	0.5304	0.4406	0.7110	0.4252
Percent of “macro” pores, %	59.1	54.1	67.5	54.6

The porosity characteristics of sample B3 can be explained by the fact that the pyrolysis in this case has been carried out at temperature, which guarantees the destruction of all the components building up the cell walls of the rice husks. The volatile degradation products are in large amount and should escape from the char without delay. This leads to the obtaining of a material with a maximum quantity of the so-called closed type of pores. The temperatures lower than 480° C, cause as a result only a slow thermal cracking of the lignin-cellulose material, which does not ensure a sufficient development of a porous structure of the obtained composite. The increasing pyrolysis temperature enhances also the effect of dehydroxylation via conversion of silanol groups to siloxane bridges leading to opening of pores. However the pyrolysis at 700° C leads to a



**Fig.6.** Characteristic integrated distribution curves of the volume and the surface area by the pore diameter for samples *B1-B4*.

complete decomposition of the organic matrix, associated with destroying of the organic-mineral structure. On the other hand thermal treatment at higher temperature causes modifications in the textural and structural characteristics of the carbon skeleton as a result of the sintering effects [34].

#### 4. CONCLUSION

Summarizing, the results evidenced that in the conditions of slow pyrolysis of rice husks the pyrolysis temperature had a strong influence on the char's structure and phase composition.

The increasing pyrolysis temperature leads to produce of composite materials, possess multi porous structure in which main part occupies the pores with size distribution between 50 and 200  $\mu\text{m}$ . While the volume of pores with a diameter less than 2.0  $\mu\text{m}$ , for the investigated temperature range remains almost the same. The pyrolysis

temperature of 480°C could be pointed as optimal for obtaining C/SiO<sub>2</sub> containing materials by slow pyrolysis of rice husks. The charcoal, obtained at this temperature is characterized with high specific surface area and advanced meso- and macroporous structure. The texture characteristics and availability of appropriate surface functionalities of sample *B3* give us the reason to expect from the sample high adsorption activity in regard to adsorption of organic and inorganic pollutants from aqueous medium.

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## ИЗМЕНЕНИЯ В СТРУКТУРАТА НА ТВЪРДИТЕ ОСТАТЪЦИ ОТ БАВНАТА ПИРОЛИЗА НА ОРИЗОВИ ЛЮСПИ

С. Узунова, Д. Ангелова, Б. Анчев, И. Узунов, А. Гигова

<sup>1</sup> Химикотехнологичен и металургичен университет, 1756 София

<sup>2</sup> Институте по обща и неорганична химия, Българска академия на науките, 1113 София

<sup>3</sup> Институт по електрохимия и енергийни системи, 1113 София

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(Резюме)

Изследването дава основата за разработването на нов екологично съобразен материал с контролирани характеристики, подходящи за производството на материали от въглерод и силициев диоксид с добавена стойност. Предмет на изследването е да се определи влиянието на температурата на пиролиза върху специфичната повърхност и порьозността на въглена, получен при бавна пиролиза в температурния интервал 250-700°C на оризови люспи, излужени с киселина. Структурата на въглена е определена с живачна порьозиметрия и BET-метода. Фазовият състав на твърдия остатък след пиролизата и отношението въглерод/силициев диоксид в него са определени чрез термичен анализ (TG/DTA/MS) и XRD. Морфологията на материала е изучен чрез сканираща електронна микроскопия. Установено е, че бавната пиролиза в изследвания температурен интервал дава твърд остатък с предимно макро-порьозна структура и разпределение на размера на порите между 50 и 200 µm. Образците, получени при 480°C се характеризират с най-голяма общ обем и най-голям среден диаметър на порите. С нарастване на температурата на пиролиза отношението C:SiO<sub>2</sub> в твърдия остатък намалява от 1.38 до 0.85, а специфичната повърхност нараства от 7.0 до 440.0 m<sup>2</sup> g<sup>-1</sup>.