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EVALUATION OF THE THERMOCHEMICAL CHANGES IN AGRICULTURAL BY-PRODUCTS AND IN THE CARBON ADSORBENTS OBTAINED FROM THEM

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Abstract

The thermochemical decomposition of waste products from a coconut (*Cocos nucifera* L.), a nut (*Juglans regia L.*) an apricot (*Armeniaca vulgaris* L.), an almond (*Amygdalus communis* L. *var amara* DC.), a grape (*Vitis vinifera* L.) and a cherry (*Prunus avium* L.), as raw materials for producing carbon adsorbents, was investigated by DTA and TG. The thermo-oxidative and decomposition processes resulting in increased number of oxygen-containing functional groups of phenolic and carbonyl type are responsible for the high adsorption capacities of the carbon adsorbents. The thermochemical changes in adsorbents based on agricultural wastes are similar to those in commercial activated carbons. The adsorbents derived from apricot stones have the highest overall thermal stability.

Keywords: carbon adsorbents, coal precursors, DTA/TG, thermo-oxidation, waste agricultural products

Introduction

The current environmental problems demand a continuous extension of the research on various raw materials relating to the production of carbon adsorbents. The use of lignocellulosic precursors for activated carbon preparation has been described [1, 2]. We previously [3–7] reported on adsorbents prepared from agricultural by-products and solid fuels by pyrolysis in a flow of water vapour. The method we developed is a one-stage combination of thermochemical decomposition processes, including carbonization of the starting materials and activation of the solid carbon product. The treatment temperature is 600–800°C.

The adsorption behavior of the carbon adsorbents is affected not only by the pyrolysis conditions and activation, but also by the chemical nature of the organic components of the original material, and its moisture and ash content. The volatile decomposition products should also be considered.

Mortly *et al.* investigated the thermal degradation and chemical characteristics of West Indian biomass (Caribbean pine, bagasse, coconut shells and coconut husks) as an active carbon product. They established that materials rich in oxygen showed higher surface area development [8].

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Puri and Barton [9, 10] studied the chemical nature of the surface of some carbon adsorbents and detected the presense of 'CO complexes' or 'CO_2 complexes'. Boehm *et al.* [11] identified and determined the carboxylic, phenolic and hydroxyl functional groups of lactone type on the carbon surface, and also proved the existence of nitrogen and sulphur bonded to the carbon skeleton.

The purpose of the present investigation was to carry out a TG/DTA study of the thermal decomposition of various waste agricultural by-products, as raw materials for carbon adsorbent preparation, and the thermal behaviour of the adsorbents obtained from them from room temperature up to 1000°C. The effects of the chemical nature of the organic compounds of the investigated products are also discussed.

Experimental

The samples comprised the following waste agricultural products: shells from almonds (*Amygdalus communis* L. *var amara* DC.) nuts (*Juglans regia* L.) and coconuts (*Cocos nucifera* L.) apricot (*Armeniaca vulgaris* L.), and cherry (*Prunus avium* L.) and grape seeds (*Vitis vinifera* L.). Furthermore, coal samples were used: lignite from the Maritza-Iztok basin (A) and from the Chukurovo seam (B) in Bulgaria. These differ in ash content (A: 5.5%; B: 20.50%) and in sulphur content (A: 0.60%; B: 1.20%). The results of chemical and elemental analyses of the raw materials are presented in Table 1.

Table 1 Chemical and elemental analysis of the raw material

No.	Material	Proximate analysis/wt%			Elemental analysis/wt%				
		Moisture	Ach	Volatile	C	H	N	S	O (by dif.)
1.	Coconut stones	5.6	0.5	76.5	49.4	6.2	0.4	0.8	43.2
2.	Nut shells	6.2	1.0	76.8	48.0	6.0	0.6	0.5	45.0
3.	Apricot stones	6.4	0.2	80.6	51.5	6.3	0.3	0.6	41.3
4.	Almond shells	6.0	0.9	82.0	46.0	5.7	0.5	0.1	48.0
5.	Grape seeds	7.6	2.6	72.3	56.0	7.0	1.5	0.1	35.5
6.	Cherry stones	6.0	0.9	82.0	54.0	7.1	0.3	0.3	38.4
7.	Coal/A/from "Maritza Iztok"	7.7	20.5	60.8	64.0	6.8	0.8	1.2	27.2
8.	Coal/B/from "Chukorovo" seam	6.4	4.5	56.6	65.0	5.3	0.5	0.6	28.5

The starting materials were subjected to pyrolysis in a flow of water vapour under conditions detailed previously [6].

The DTA analyses were performed on a Q 1500 derivatograph (MOM, Hungary), under the following conditions: heating rate 10°C min^{-1}, static atmosphere, ceramic crucible, Al_2O_3 as reference, and samples with a particle size of 0.1–0.3 mm.

The contents of the various functional groups were determined as follows: OH groups with barium hydroxide and C=O groups with hydroxylamine hydrochloride [12]. Cellulose was determined by the nitrogen-alkaline method of Nikitin [13] and lignin by the well-known procedure of Koning [13]. Holocellulose was analysed by applying sodium chloride in an acetic acid medium [13].

The adsorption capacities of the carbon adsorbents were determined with respect to iodine adsorption [14]. The specific surface areas of the adsorbents were estimated via the volume of adsorbed nitrogen [15].

Results and discussion

The chemical compositions of these samples of plant origin show them to be products of lignocellulosic character (Table 2). Holocellulose contains cellulose, pentosanes, hexosanes and polyuronic acids. The bonding of cellulose to lignin substructures and all remaining compounds (defining the structure of the plant samples) involves the formation of H-bonds between cellulose and other polysaccarides, complexing with metals and the formation of complex compounds with proteins and lipid structures. Since coals result from the coalification of plant products, it was interesting from both practical and theoretical points of view to compare their thermochemical behaviour with that of waste agricultural products.

The TG data on the initial materials of plant origin and on selected coal samples reveal a multistage thermochemical decomposition process (Table 3, Fig. 1). The mass loss between 110 and 120°C is due to dehydration processes. The differences between the mass loss (%) in this temperature range (Table 3) and the moisture content (%) of the initial samples (Table 1) are associated with the existence of various structures and forms of water bonding.

The DTA curves of samples from coconut and nut shells (Fig. 2, Nos 1 and 2) display exothermic peaks at 180 and 150°C. These low-temperature thermochemical processes take place without any significant mass change (Fig. 1a, Nos 1 and 2) and can be attributed to the presence of oxidative unstable cellulosic fragments and to the breaking of ester and ether bonds. The DTA curves of samples of apricot, almond, cherry and grape, and also the coal samples, do not exhibit thermal effects in the temperature range 120–200°C and the mass losses are insignificant: up to 2%.

Table 2 Chemical characteristics of the raw material

No.	Material	Cellulose/ wt%	Lignine/ wt%	Holocellulose/ wt%	Pentosans, hexosans andpolyuronic acids, wt%
1.	Coconut stones	20	30	68.8	48.8
2.	Nut shells	40	39	59.0	19.0
3.	Apricot stones	30	37	58.0	28.0
4.	Almond shells	20	34	62.0	42.0
5.	Grape seeds	30	49	48.0	18.0
6.	Cherrystones	28	40	55.0	27.0

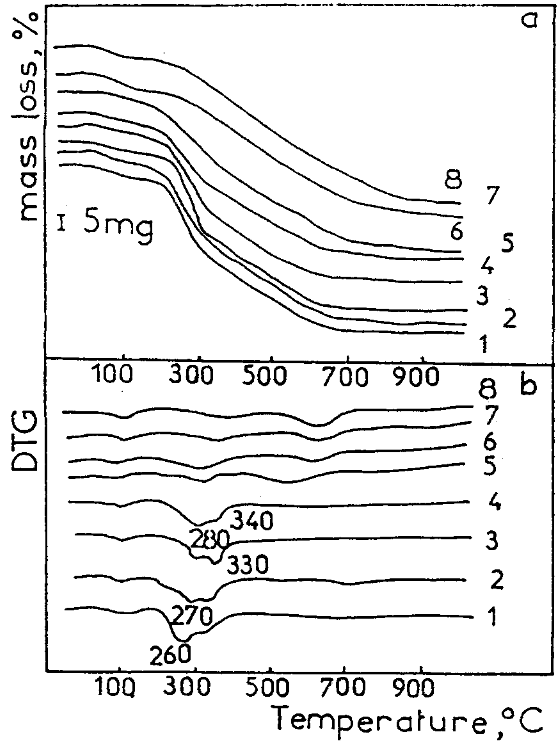

Fig. 1 Thermal decomposition of agricultural by-products and coal (a/TG curves; b/DTG curves): 1) coconut stones; 2) nut shells; 3) apricot stones; 4) almond shells; 5) grape seeds; 6) cherry stones; 7) coal from 'Maritza Iztok' seam; 8) coal from 'Chukurovo' seam

The volatile products from the samples of plant origin are evolved at temperatures higher than 220°C. This process is demonstrated by the TG curves (Fig. 1a). It is well known that the thermochemical processes include numerous parallel and competitive reactions due to the heterogeneity in chemical composition of the samples studied. Hence, it is inappropriate to evaluate any definite relationship between the percentage decrease in mass and the variations in chemical composition, or to propose an operative mechanism. Generally, after dehydration of the lignocellulosic products, the number of C=O bonds is increased [16]. The thermochemical changes in this temperature range may be attributed to the participation of C=O and carboxyl groups. This observation is in agreement with results from other studies on products with similar composition [17]. The variety of the bonding of the volatile components is confirmed by the differences in the rates of thermal degradation: the temperature maxima, as shown in the DTG curves, appear in the temperature range 260–340°C (Fig. 1b). The thermally initiated oxidative and degradation reactions take place at temperatures higher than 270°C and the thermal effects are revealed by the appearance of exothermic peaks at 270–380°C (Fig. 2).

Table 3 Thermal decomposition data of the raw material

No.	Material	Stage I		Stage II		Stage III		Residue/ %
		Temperature interval*/°C	Mass loss/ %	Temperature interval/°C	Mass loss/ %	Temperature interval/°C	Mass loss/ %	
1.	Coconut stones	to 110	6	110–340	46	340–680	44.0	4.0
2.	Nut shells	to 120	4	110–350	46	350–690	45.5	4.5
3.	Apricotstones	to 110	6	110–350	48	350–670	44.0	2.0
4.	Almondshells	to 120	8	120–360	52	360–675	38.0	6.0
5.	Grape seeds	to 110	4	120–380	45	380–770	46.0	5.0
6.	Cherrystones	to 120	4	120–380	45	380–680	31.0	20.0
7.	Coal/A/from ‘Maritza Iztok’ seam	to 110	4	110–350	11	350–780	75.5	4.0
8.	Coal/B/from ‘Chukorovo’ seam	to 120	4	120–350	16	350–870	72.0	8.0

* from ambite temperature

As concerns lignin, it has been shown that major changes in the decomposition of wood lignin take place in the temperature range 450–500°C [17]. Arima [18] reported that the thermal degradation of lignin is dependent on its bonding with the remaining components. The thermochemical changes in the samples studied take place without any distinct variations in the decomposition rate above 400°C (Fig. 1b). It should be noted that no enthalpy changes were observed in the DTA curves in the temperature range 400–580°C (Fig. 2).

The condensation processes are accelerated at temperatures higher than 400°C [18] and result in an increased content of aromatic clusters in the samples of plant origin. The thermal effects in the temperature range 600–770°C are due to the thermochemical changes in the polycondensation products.

Analysis of the TG/DTA data on the various samples of plant origin led to the following findings:

1) The thermochemical variations in the samples from coconuts, nuts, apricots and almonds are similar. The exothermic peaks in the temperature range 300–380°C are associated with active pyrolysis of the cellulosic fragments.

2) The thermochemical changes in cherry stones and in grape seeds occur at higher temperatures (Fig. 2, Nos 5 and 6). These results may be due to the lower content of oxidized lignocellulosic fragments [16] or to the higher lignin content (Table 2).

3) The exothermic effects at temperatures higher than 600°C are attributed to the thermochemical changes in the carbonized products.

4) The DTA and TG data appear to be insufficient to allow determination of the relative proportions of the two main biopolymer families: lignin and cellulose.

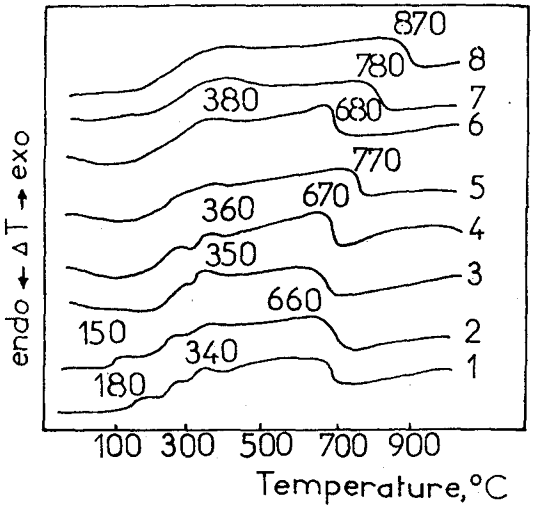

Fig. 2 Thermochemical destruction of agricultural by-products and coal: 1) coconut stones; 2) nut shells; 3) apricot stones; 4) almond shells; 5) grape seeds; 6) cherry stones; 7) coal from 'Maritza Iztok' seam; 8) coal from 'Chukurovo' seam

We observed significant changes during the thermochemical decomposition of coal samples. The DTA data show that the enthalpy changes are shifted to higher temperatures (Fig. 2, Nos 7 and 8), which is due to the presence of thermally stable products in them. The major mass losses are observed in the temperature range 350–870°C for the sample from the Chukurovo seam, and 350–780°C for that from the Maritza-Iztok basin (Table 3). The results show that sample B, which is characterized by lower contents of sulphur and ash is thermally the more stable.

Adsorbents with a strongly developed porous surface were obtained as a result of the physical and chemical changes in the initial raw materials by pyrolysis in a flow of water vapour. Their adsorption and technical characteristics are summarized in Table 4. The reaction properties of the adsorbents depend on their thermal stability and on the thermochemical changes which they undergo at various temperatures. The data in Table 5 show that the thermal destruction of the active carbons proceeds in three stages. The mass loss during the first stage (up to 100°C) is due to the evaporation of adsorbed moisture. The absence of volatile products is proved by the minimal mass loss registered during the second stage of thermal decomposition (Table 5). The adsorbent from apricot stones appears to be the most thermally stable product. This is proved by the very low mass loss in the temperature range 100–400°C (only up to 1%) (Table 5, No. 3) and the exothermic peaks observed at 530 and 990°C (Fig. 3, No. 3). This is most probably due to the intense chemical processes which are responsible for the formation of a porous structure in the solid residue. The X-ray data show that the active carbon from apricot stones has a poorly-ordered structure, as evidenced by the presence of microcrystalline structures [7]. This is characteristic of high-quality adsorbents (Table 4, $V=$ 1175 m^2g^{-1}).

The DTA results suggest that the major thermochemical changes in the carbon adsorbents from coal samples and from agricultural wastes take place in the temperature range 390–580 and 860–990°C, respectively. The thermal decomposition processes in the adsorbents proceed during the third stage (Table 5). Comparison of the thermal stabilities of the adsorbents we obtained and commercial activated carbon revealed that the most thermally stable carbon adsorbents are those from apricot stones and Chukurovo seam coal (Table 5, Nos 3 and 8). We failed to observe significant differences between the thermal decomposition processes for the other adsorbents and the standard samples.

The reactivities of the adsorbents also depend on the content of oxygen functional groups in the initial materials [18] and their thermochemical changes during pyrolysis in a flow of water vapour. The functional analysis results show significant increases in the contents of OH and C=O groups in the carbon adsorbent as compared with those for the initial samples (Fig. 4). It should be pointed out that the increases in the concentrations of OH and C=O groups in the carbon adsorbents from shells of coconut and nut are much higher than for the others. These results, together with the low-temperature exo-peaks (Fig. 2, 150 and 180°C), indicate the presence of less oxidatively stable lignocellulosic fragments in these samples and the occurrence of thermo-oxidative processes. The smallest changes in the content of oxy-

Table 4 Characteristics of the carbon adsorbents

No.	Material	Proximate analysis/wt%			Adsorption capacity towards iodine*/mg g^{-1}	Specific surface area/m^2 g^{-1}
		Moisture	Ach	Volatyl		
1.	Coconut stones	1.3	2.4	4.9	878	700
2.	Nut shells	4.0	3.1	7.0	683	904
3.	Appricot stones	1.6	2.0	3.7	894	1175
4.	Almond shells	2.3	2.7	3.3	677	946
5.	Grape seeds	1.8	13.5	4.4	823	900
6.	Cherry stones	1.9	4.2	9.9	677	836
7.	Coal/A/from “Mariza Iztok” basin	2.0	31.6	6.0	400	345
8.	Coal/B/from “Chukorovo” seam	2.3	10.4	7.9	662	904

*Adsorption capacity towards iodine: Chemvitron C XII–663 mg g^{-1}; Degusawt I–946 mg g^{-1}; Germany AS–693 mg g^{-1}; Norit R–BX–S–1–992 mg g^{-1}.

Table 5 Thermal decomposition data of carbon adsorbents

No.	Material	Stage I		Stage II		Stage III		Residue/%
		Temperature interval*/°C	Mass loss/%	Temperature interval/°C	Mass loss/%	Temperature interval/°C	Mass loss/%	
1.	Coconut stones	to 100	8	100–300	2.0	300–965	90.0	–
2.	Nut shells	–100	5	100–300	1.5	300–990	87.9	5.6
3.	Apricot stones	–100	6	100–400	1.0	400–990	85.0	8.0
4.	Almond shells	–100	8	100–250	–	250–920	78.0	15.0
5.	Grape seeds	–100	4	120–300	2.0	310–980	80.0	12.0
6.	Cherry stones	–100	8	100–310	2.0	300–930	69.0	21.0
7.	Coal/A/from 'Mariza Iztok' seam	–100	1	100–350	2.0	350–965	82.6	15.4
8.	Coal/B/from 'Chukorovo' seam	–100	–	100–370	1.0	370–860	52.0	47.0
9.	Chemivitron C XII	–100	12	100–280	1.0	280–980	87.0	–
10.	Degusawt I	–100	4	100–330	2.0	300–100	94.0	–
11.	Germany AS	–100	10	100–380	6.0	380–990	84.0	–
12.	Norit R–BX–S–1	–100	4	100–450	4.0	450–1000	92.0	–

*from ambite temperature

gen bonded in OH and C=O groups are observed for the samples of grape seeds (Fig. 4, No. 5). These results are due to the high lignin content (Table 2) and are in agreement with the DTA data: the appearance of an exo-effect at 770°C (Fig. 2, No. 5).

The highest intensity of the thermo-oxidative processes during pyrolysis with water vapour was observed for the apricot stone samples. The increase in C=O oxygen content was 12.3-fold and the content of OH groups in the carbon adsorbent was relatively low (Fig. 4, No. 3). The DTA curves exhibit relatively high-temperature exopeaks in the derived carbon adsorbent (compare Fig. 2, No. 3 with Fig. 3, No. 3).

The content of C=O oxygen increased significantly for the sample from cherry stones (Fig. 4, No. 6). The high content of OH groups both in the initial material and in the adsorbent obtained suggests the presence of fragments stable to oxidation.

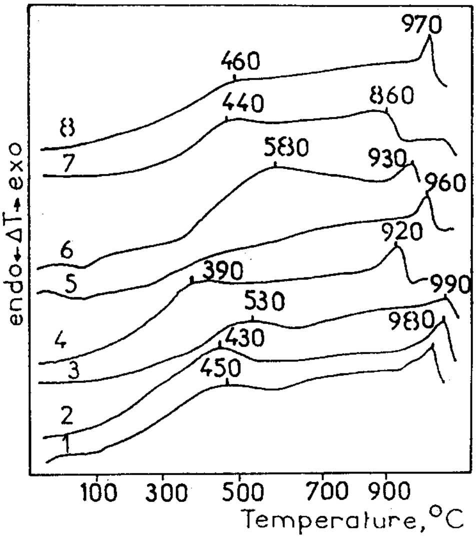

Fig. 3 Thermochemical decomposition of carbon adsorbents obtained from: 1) coconut stones; 2) nut shells; 3) apricot stones; 4) almond shells; 5) grape seeds; 6) cherry stones; 7) coal from 'Maritza Iztok' seam; 8) coal from 'Chukurovo' seam

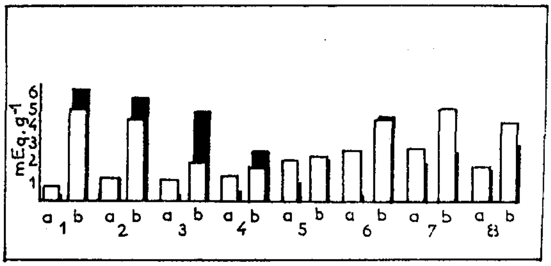

Fig. 4 Oxygen-containing functional groups in raw materials (a) and in derived adsorbents (b): 1) coconut stones; 2) nut shells; 3) apricot stones; 4) almond shells; 5) grape seeds; 6) cherry stones; 7) coal from 'Maritza Iztok' seam; 8) coal from 'Chukurovo' seam. ☐-OH groups; ■-C=O groups

The coal samples are characterized by a higher content of OH oxygen as compared with C=O oxygen (Fig. 4).

The functional analysis and DTA data lead us to conclude that the mechanism of the thermo-oxidative processes during pyrolysis with water vapour exerts a significant effect on the carbon adsorbents obtained from materials with lignocellulosic compositions. This is proved by the following major observations:

a) an increase in the oxygen-containing functional groups in the carbon adsorbents as compared with those of the initial materials;

b) an increase in the content of C=O oxygen in the adsorbents from agricultural wastes.

The functional analysis data show that the content of C=O oxygen in the adsorbent from apricot stones is 12.3 times higher than that of OH oxygen. This is not observed for the other cases. The dynamics of changes in oxygen-containing functional groups reveal their active participation in the polycondensation process and in the packing of the carbon skeleton of the adsorbents. This results in an increase of their thermal stability. The oxygen-containing functional groups most probably participate in the formation of condensed rings with the oxygen heteroatom.

Conclusions

1. DTA and TG methods were used to investigate the thermochemical decomposition of several waste agricultural products as raw materials for carbon adsorbent preparation. It was established that the major changes in the thermochemical variations occur in two temperature intervals: 110–380°C and 650–770°C. These data can be used for determination of the pyrolysis conditions.

2. It was found that the intensive thermo-oxidative decomposition processes result in an increase in the content of oxygen-containing functional groups of phenolic and carbonyl type and strongly influence the adsorbent capacity.

3. The thermochemical changes in these adsorbents obtained from agricultural wastes take place in the temperature ranges 390–580°C and 860–990°C and are similar to those in commercial active carbon. The adsorbents from apricot stones display the highest thermal stability, which is due to the specific structure of the carbon skeleton.

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