Journal of Thermal Analysis and Calorimetry, Vol. 63 (2001) 855–863

APPLICATION OF THERMAL ANALYSIS TO THE STUDY OF SOME WASTE AGRICULTURAL PRODUCTS FOR THE PREPARATION OF ACTIVE CARBONS

T. Lupascu[1], *I. Dranca*[1], *V. T. Popa*[2] *and* *M. Vass*[2]

[1]Institute of Chemistry, Academy of Sciences of Moldova, Str. Academiei 3, Chisinau MD-2028, Republic of Moldova
[2]Romanian Academy, Institute of Physical Chemistry, Spl. Independentei 202, 77208 Bucharest, Romania

(Received April 2, 2000; in revised form November 30, 2000)

Abstract

TG, DTG and DTA methods were used for the investigation of some waste agricultural products, such as grape seeds, walnut shells, plum and peach stones, which can serve as raw materials for the production of active carbons. It was demonstrated that thermoanalytical methods are appropriate to study the thermal characteristics of the above wastes and the data obtained can be applied to the technological processes of active carbon preparation.

Keywords: active carbons, thermal analysis, waste agricultural products

Introduction

An important area of the application of some waste agricultural products is their utilization as raw materials for the preparation of active carbons. Active carbons (*AC*) are useful materials in fields such as adsorption of different substances from gaseous and liquid phases, purification of various categories of wastewater, food processing and technology. *AC*s are also used in medicine for the removal of toxic substances from biological solutions, including blood detoxification (as haemosorbents).

The proposed goals of the present study are rather infrequent in thermal analysis (TA), but despite of it there are data demonstrating that TA methods can be used in the research of similar products. For example, Edmonds *et al.* [1] investigated the thermal behavior of tobacco leaves, and Arseneau [2] applied DTA methods to the studies of dry pinewood as well as wood samples of this tree submitted to different solvents extraction procedures: water–ethanol, benzene–ethanol, etc. Thermal analysis methods were also applied for quantitative characterization and estimation of the possibility to use some waste agricultural products (wheat and rye straw, grape stems) as fuel. The thermal degradation of the above samples takes place in 4 stages.

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

The first one is due to processes of dehydration (30–110°C); the second is characterized by burning of volatile products (110–320°C). The burning of lignocellulose products occurs in the temperature range 320–530°C, and no mass changes are observed within the temperature range 530–900°C [3]. Shopova *et al.* [4] investigated thermochemical decomposition of different waste agricultural products: coconut shells, almond and apricot stones and the active carbons produced from them. It was found that the thermal parameters of the prepared active carbons are similar to those of commercially available active carbons. Important characteristics of the ignition process such as spontaneous ignition temperature (*SIT*) and point of initial oxidation (*PIO*) were evaluated for, among others, coconut shell carbons by Suzin *et al.* [5]. The adsorption properties of surface groups obtained via carbon dioxide, steam, and air activation was studied by Molina-Sabio *et al.* [6] for peach and plum stone carbons and by Toles *et al.* [7] for a variety of nutshell carbon. An extensive FT-IR study of surface oxygen structures resulted from different activation procedures on cherry stone carbons was performed by Gomez-Serrano *et al.* [8].

The goal of the present research is to investigate thermal characteristics of some waste agricultural products, to determine optimum parameters of carbonization of the fruit stones and grape seeds using thermal analysis methods, and to assess thermal characteristics of the carbons produced from the raw materials.

Experimental

TG, DTG and DTA methods were applied to the investigations of grape seeds, peach and plum stones, and walnut shells which were preliminarily cleaned, washed and dried at room temperature. As an alternative to the technique of carbonization, the peach stones were treated with K_2CO_3 and $KHCO_3$ solutions.

The conditioning of raw materials and the standard carbonization procedure leading to their corresponding carbons were previously described [9]. Throughout the present study grains with a mean size of approximately 2 mm were used for both types of samples.

The thermoanalytical measurements were performed on a Derivatograph OD-102 system Paulik–Paulik–Erdey (MOM, Budapest) in ambient atmosphere. Sample mass was 50 mg, resolution of TG 50 mg, of DTA 1/5, of DTG 1/10, heating rate 10°C min^{-1}, temperature range 20–1000°C. α-alumina was used as inert material.

A computer interfaced DuPont 1090 Thermal Analyzer with a 951 TG thermobalance was used for the measurements in CO_2, (technical grade, dried over silicagel and molecular sieves) with a flow rate of 50 ml min^{-1}. Experimental conditions were the following: the temperature range 25–700°C was swept with a heating rate of 10°C min^{-1}, followed by an isothermal regime for 60 min. Sample mass was 50 mg and data were stored with a sampling rate of 3 s/point. Mass changes, temperatures and residues were evaluated by means of the TG Data Analysis v.1.0 program.

TG and DTG runs for the basic raw materials and two alkali-pretreated samples, in ambient atmosphere, are illustrated in Fig. 1, which displays TG and DTG curves, and Fig. 2, which presents DTA signals. All curves were vertically shifted for a better visualization of differences in the thermal behavior of different samples. TG runs in CO_2 atmosphere are given in Fig. 3, for raw materials, and Fig. 4, for the corresponding carbons, respectively. Within these last two figures TG curves are presented on the same scale, which better illustrates both similarities and differences in the thermal behavior of the investigated samples.

Results and discussion

The results of the elemental analysis [9] of the basic materials under study are presented in Table 1. The elemental composition of grape seeds singles out among the investigated materials: this is the only raw material with a significant nitrogen content, which is reflected in the thermal behavior of this sample under both ambient and carbon dioxide atmospheres. For the other samples there are slight differences in C, O, H content, and N is absent.

Table 1 Results of elemental analysis of raw materials

Raw material	C/%	H/%	N/%	O/%
Grape seeds	50.14	7.07	1.94	40.85
Walnut shells	47.63	6.04	–	45.33
Plum stones	46.85	6.47	–	46.88
Peach stones	43.91	5.73	–	50.36

Table 2 summarizes the results of the derivatographic analysis, in air, of the raw materials used in the preparation of the active carbons (*AC*). All basic raw materials exhibit four temperature ranges, more or less well evidenced, with significant mass losses. For the treated samples this pattern does not change. However, there are important changes that affect both temperature ranges and the corresponding mass losses, as well as the final residues: the ash content of the treated samples is higher than that of the basic raw material, as expected.

The analysis of the TG, DTG and DTA curves given in Figs 1 and 2 and the results presented in Table 2 suggest that the process of the thermal decomposition of the initial products in air comprises mainly 4 stages: 1. the first one, which begins at about 30 and ends at about 150°C can be ascribed to dehydration; 2. Exothermal effects are observed on the DTA curves for the materials studied in the temperature range 150–300°C are rather difficult to identify. They probably pertain to complex oxidative degradations of the organic matter, with moderate overall mass losses. 3–4. Extended exothermal effects and mass losses are observed within the temperature interval 350–700°C: they could be confidently ascribed to the carbonization and burning of lignocelluloses constituents which takes place in two more or less well evidenced stages, manifested in one/both of DTG or/and DTA curves. With the exception of $KHCO_3$ treated peach stones, no significant mass losses were found at temperatures higher than 700°C. This was the main reason in the choice of this isothermal temperature for the runs performed in CO_2 atmosphere.

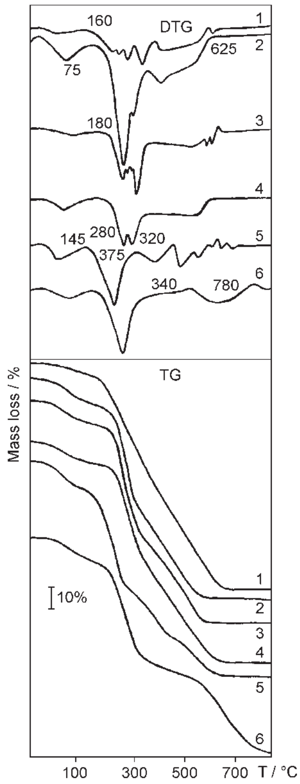

Fig. 1 TG and DTG (MOM OD-102) of raw materials in air: 1 – grape seeds; 2 – walnut shells; 3 – plum stones; 4 – peach stones; 5 – peach stones with K_2CO_3, 6 – peach stones with $KHCO_3$

The dramatic change in the shape of the thermoanalytical curves of the peach stones saturated with K_2CO_3 and $KHCO_3$ (Figs 1 and 2) demonstrate that this treatment results in major changes in the processes of thermal degradation. These effects are supposed to be caused by the modifications in the initial material structure and by a catalytic effect in the onset of carbonization. As expected, ash content increased for these two samples.

The thermal behavior of raw materials and their corresponding carbons in CO_2 atmosphere was studied on a 1090 DuPont Thermal Analyzer. TG curves are illustrated in Fig. 3 (raw materials) and 4 (carbons), while quantitative aspects of the observed processes are summarized in Tables 3 and 4, respectively.Major differences between the two sets of experiments (in air and carbon dioxide) are evidenced, as expected: while TG curves in air represent an overall process of burning, those in CO_2 reflect an overall process of carbonization. With the notable exception of grape seeds, in carbon dioxide atmosphere the number of stages (temperature ranges with sizable mass losses) is reduced to three and the much higher residues no longer represent ash but rather carbon. The open balance of percentages presented in Table 3 is due to the

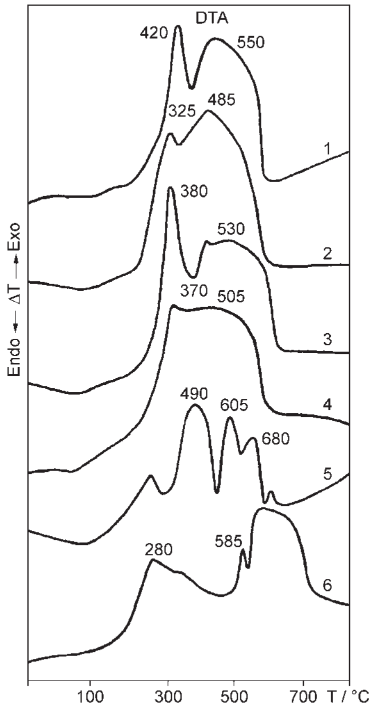

Fig. 2 DTA (MOM OD-102) of raw materials in air: 1 – grape seeds ; 2 – walnut shells; 3 – plum stones; 4 – peach stones; 5 – peach stones with K_2CO_3; 6 – peach stones with $KHCO_3$

small isothermal mass loss (60 min at 700°C), which was not explicitly given. The singled-out behavior of grape seeds is most probably due to their special structure and composition, as reflected in the elemental analysis, Table 2, by the sizable nitrogen content. Meanwhile, all other materials exhibit quite similar TG curves and residue sizes.

The first stage (approx. 25–200°C) again represents sample dehydration, with a considerable lower magnitude in grape seeds. The second and third ones (approx. 200–330 and 330–700°C) pertain to thermal degradation and carbonization of the organic material, with carbon dioxide acting as an almost inert gas. In the case of grape seeds this process seems more complicated, as the temperature range 200–700°C comprises three well-defined stages.

Carbon dioxide action becomes sizable over 700°C and consists mainly in a surface attack of the already formed carbon. As shown by Gomez-Serrano *et al.* [8] for cherry stones carbons, no new oxygen surface groups are formed through this process, in accordance with Zawadski [10], which showed that CO_2 activation of carbon films at 600°C yields no surface functional groups with acidic character.

Table 2 Thermoanalytical results (TG, DTG, DTA in air) for raw materials used in the preparation of active carbons

Raw material	ΔT/°C	Mass loss/%	ΔT/°C	Mass loss/%	ΔT/°C	Mass loss/%	ΔT/°C	Mass loss/%	Residue/%
Grape seed	45–160	4.0	160–370	35.0	370–460	17.0	460–710	42.0	2.0
Walnut shell	30–165	11.0	165–320	44.0	320–375	10.0	375–625	33.0	2.0
Plum stone	40–180	9.5	180–320	36.0	320–420	21.0	420–700	32.0	1.5
Peach stone	30–160	10.0	160–300	22.0	300–370	24.0	370–640	43.0	1.0
Peach stone K_2CO_3	35–145	11.0	145–375	48.0	375–580	20.0	580–760	16.0	5.0
Peach stone $KHCO_3$	40–160	11.0	160–340	43.0	340–620	25.0	620–780	15.0	6.0

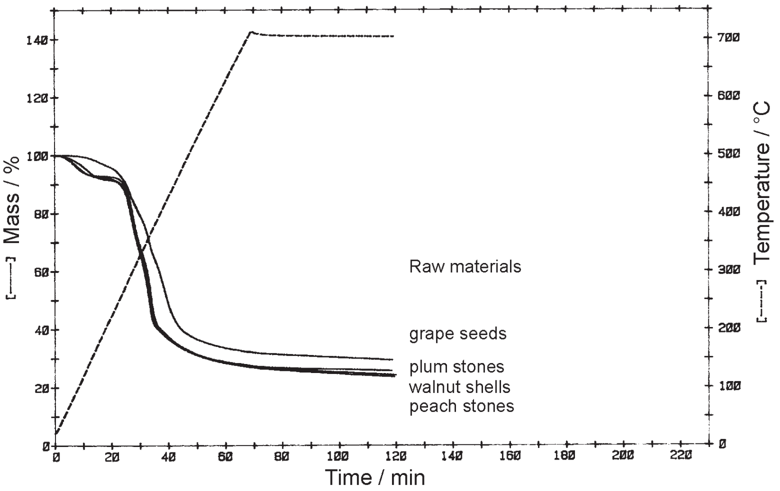

Fig. 3 TG in CO_2 (DuPont 1090) of basic raw materials

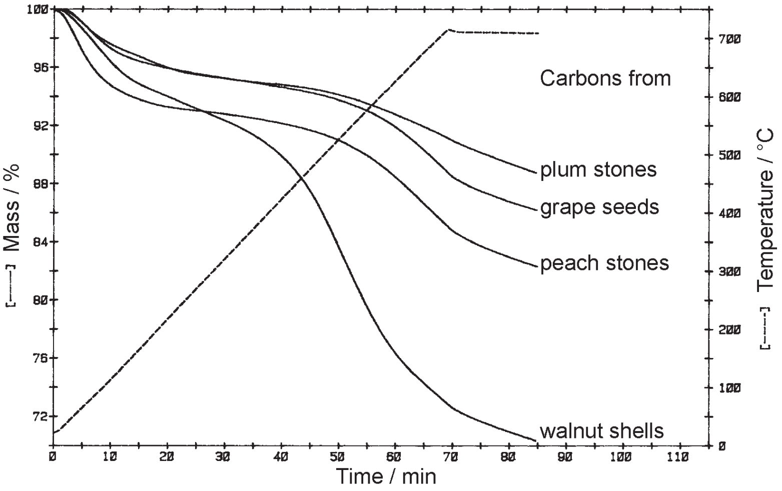

Fig. 4 TG in CO_2 (DuPont 1090) of corresponding carbons

Table 3 Thermogravimetric results (DuPont 1090 TG in CO_2) for raw materials

Raw material	ΔT/°C	Mass loss/%	ΔT/°C	Mass loss/%	ΔT/°C	Mass loss/%	Residue (C)/%
Grape seeds	25–205	3.6	210–320 320–380	16.0 16.6	380–700	31.6	29.4
Walnut shells	25–200	7.6	200–325	24.2	325–700	43.7	23.8
Plum stones	25–225	8.5	225–340	27.4	340–700	37.5	25.7
Peach stones	25–185	7.1	185–330	26.5	330–710	39.8	24.0

Table 4 Thermogravimetric results (DuPont 1090 TG) of thermal behavior in CO_2 of carbons produced from raw materials

Initial raw material	ΔT/°C	Mass loss/ %	ΔT/°C	Mass loss/ %	Residue (carbon)/%
Grape seeds	25–275	4.5	275–700	12.1	83.4
Walnut shells	25–250	6.3	250–700	26.8	66.9
Plum stones	25–225	4.0	225–700	10.6	85.4
Peach stones	25–280	7.2	280–710	14.8	78.0

Contrasting to the above-presented results, carbons obtained through a standard procedure [9] from the basic raw materials under study exhibit different features. Their behavior in CO_2 is illustrated qualitatively by TG curves in Fig. 4 and summarized quantitatively in Table 4. Differences among samples are more pronounced than in the case of raw materials, especially in the values of residues. There are two well distinguishable stages: 1. volatiles desorption within approx. 25–250°C and 2. two overlapping processes consisting in further carbonization and CO_2 surface action within approx. 250–700°C, which continues within the isothermal portion of the run. In contradistinction with the corresponding raw materials, CO_2 surface attack seems more important in the case of carbons. Here walnut shells single out, with a considerable lower residue, which indicates that carbonization is not complete through the standard procedure [9] for this sample. For this material there is a clear indication of some bulk, rather than surface processes taking place upon heating in carbon dioxide atmosphere. This agrees with the findings of Toles *et al.* [7], which proved, on a large variety of nutshells, that the type of nutshell used for activated carbon production has little effect on the types of functional groups obtained.

Conclusions

Thermal properties of some agricultural waste by-products (grape seeds, plum and peach stones and walnut shells) and their corresponding carbons were studied by means of derivatograph (TG, DTG, DTA) in air and thermogravimetric analysis (TG) in carbon monoxide.

The results of the research demonstrate that the initial materials differ in thermal behavior in ambient atmosphere. However, their TG curves in carbon dioxide are quite similar, with the exception of grape seeds. One may infer that, despite their different origin and structure, walnut shells and plum and peach stones closely resemble with respect of their carbonization process in CO_2. Meanwhile, the different chemical nature and texture of raw materials result in their different burning properties. Grape seeds' behavior in both experiments singles out, and is most probably related to the sizable nitrogen content of this sample, as evidenced in the elemental analysis.

Carbons originated from the above raw materials (through standard procedures [9]) were submitted to carbon dioxide activation, within a thermal treatment identical to that applied to their parent stuff. TG curves are quite different for the investigated samples, with an ongoing carbonization process, especially for the walnut shell carbon. The surface action (attack) of carbon dioxide at 700°C is more pronounced for these carbons than the one taking place on ‘in situ carbons’, produced during the calcination of raw materials in CO_2.

References

1 M. D. Edmonds, M. C. Core, A. Barley and R. F. Schwenker, International Weekly Tobacco, 1600 (1965) 28.
2 D. F. Arseneau, Can. J. Chem., 39 (1961) 1915.
3 P. J. Rey, J. Martin Gil, M. A. Villaman and J. San Jose, J. Thermal Anal., 40 (1993) 239.
4 N. Shopova, V. Minkova and K. Markobe, J. Thermal Anal., 48 (1997) 309.
5 Y. Suzin, L. C. Buettner and C. A. LeDuc, Carbon, 37 (1999) 335.
6 M. Molina-Sabio, M. A. Munecas-Vidal and F. Rodrigues-Reinoso, Characterization of Porous Solids II, Elsevier, Amsterdam 1991, p. 329.
7 C. A. Toles, W. E. Marshall and M. M. Johns, Carbon, 37 (1999) 1207.
8 V. Gomez-Serrano, F. Piriz-Almeida, C. J. Duran-Valle and J. Pastor-Villegas, Carbon, 37 (1999) 1517.
9 T. Lupascu, L. Monahova and V. Gonchar, Revue Romaine de Chimie, 39 (1994) 909.
10 J. Zawadski, Chemistry and Physics of Carbon, Vol. 21, P. A. Thrower, Ed., Marcel Dekker, New York 1989, pp. 147–380.