Journal of Thermal Analysis and Calorimetry, Vol. 63 (2001) 351–357

THERMOGRAVIMETRIC ANALYSIS OF CORN COB IMPREGNATED WITH ZINC CHLORIDE FOR PREPARATION OF ACTIVATED CARBON

W. T. Tsai[1], *C. Y. Chang*[2], *S. L. Lee*[2] *and S. Y. Wang*[2]

[1]Department of Environmental Engineering and Health, Chia Nan University of Pharmacy and Science, Tainan 717, Taiwan
[2]Graduate Institute of Environmental Engineering, National Taiwan University, Taipei 106, Taiwan

(Received March 27, 2000; in revised form August 13, 2000)

Abstract

The thermochemical decomposition of agricultural by-product corn cob impregnated with $ZnCl_2$, as a precursor material for producing the activated carbons, was investigated by thermogravimetric (TG) analysis at the heating rate of 5 and 10°C min^{-1} under a controlled atmosphere of nitrogen (60 ml min^{-1}). The appearance of a peak in the differential thermogravimetric plot (DTG) in the temperature range of 400–600°C is significantly related to the extent of impregnation. The DTG curve of the sample impregnated with the optimal impregnation ratio of 175% (i.e., the ratio of $ZnCl_2$ mass of 87.5 g in the 200 cm^3 of water to corn cob mass of 50 g), which yields an optimal BET surface area of the activated carbon and displays a DTG peak at about 500°C. This may be partially due to the intense chemical activation and results in the formation of a porous structure in the activated solid residue. This observation is also in close agreement with previous results at optimal pyrolysis temperatures of 500°C and with similar experimental conditions. In order to support the results in the TG-DTG analysis, the development of pore structure of the resulting activated carbons thus obtained by previous studies was also examined and explained using the scanning electron microscopy (SEM).

Keywords: activated carbon, chemical activation, corn cob, SEM, TG-DTG, zinc chloride

Introduction

For every 100 kg of corn grain, approximately 18 kg of corn cob is produced [1]. A large amount of corn cob is thus generated and remains unused as cellulosic wastes in fields and factories. This poses a serious problem not only in storage but also for disposal. It was noted that the utilization of this agricultural by-product as raw materials for the productions of energy [2], chemicals [3] and activated carbons [4, 5] has increased notably in recent years. It was reported that the adoption of combustion is one of the main choices to treat this renewable energy source as a fuel in Taiwan [6]. However, this method will need a proper control of air pollution generated from burn-

1418–2874/2001/ $ 5.00
Akadémiai Kiadó, Budapest

ing in the open field and farmhouse. Conversion of lignocellulosic wastes by thermochemical methods, particularly the pyrolysis, as the precursor materials for the activated carbon preparation has been widely reported in the literature [5, 7]. The chemical properties of corn cob, i.e., the ash and carbon content [8], indicate that it is a suitable carbonaceous material for the production of activated carbon.

In previous work [5, 9], it was demonstrated that the chemical activation of corn cob with zinc chloride ($ZnCl_2$) was suitable for the preparation of activated carbons which are essentially microporous. It was also illustrated that the optimal condition of operating pyrolysis temperature for the production of activated carbon with high surface area (>1400 $m^2\ g^{-1}$) is about 500°C when the experiments were performed at a pre-pyrolytic heating rate of 10°C min^{-1} under an atmosphere of flowing nitrogen, which is consistent with the results of other researches [10–13]. It was also found that the BET surface areas and the total pore volumes of the resulting activated carbons increase rapidly with increase in the impregnation ratio (R_i; i.e., the ratio of $ZnCl_2$ mass of 0–87.5 g in the 200 cm^3 solution to corn cob mass of 50 g) up to 175%.

The main purpose of the present investigation was to carry out a thermogravimetric (TG) analysis study of the thermal decomposition of the agricultural waste corn cob impregnated with $ZnCl_2$ as the chemical activator for the carbon adsorbent preparation. This would make it possible to obtain the criteria for the selection of appropriate operating parameters in the instrumental analyses prior to the chemical activation experiments. Therefore, the rate of degradation of the impregnated samples were studied by the differential thermogravimetry (DTG) to relate the effects of pyrolysis temperature and impregnation ratio on the physical properties of the activated carbons obtained in the previous work [5, 9]. In order to elucidate the TG-DTG information on pore development in the $ZnCl_2$ activation, the pore textures of the starting material and the activated carbons obtained previously [5, 9] were further examined and explained using the scanning electron microscopy (SEM).

Experimental

Preparation of sample

Dry corn cob, which was crushed, separated from its pitch/chaff and sieved to mesh range of 12×16 (average particle diameter of 1.44 mm), was used in the present study. The results (unit: mass%) of elemental and proximate analysis of the raw materials are presented as follows: C 46.8, H 6.0, N 0.9, O (by difference) 46.3 [9], and moisture 4.3, volatile organics 78.7, fixed carbon 16.1, ash 0.9, respectively. It is noted that the atom ratio of the contents of elements C, H and O of corn cob is of 12:18:8, which is characteristics of its cellulose and hemicellulose textures [1, 14]. Also, corn cob was proposed to use as a prospective starting material for the preparation of activated carbon because of its relatively high fixed-carbon content, low ash content and the presence of inherent porous structures. The precursor materials were washed by the distilled water in order to reduce the residues content. They were then dried at 105°C for at least 12 h, before using in the impregnation of corn cob with $ZnCl_2$ solu-

tion. Impregnation was carried out as follows: 50 g dried corn cob was mixed in a glass flask with 200 cm^3 of $ZnCl_2$ solutions of various Ri. Then the solution was stirred and heated on a hot plate/magnetic stirrer to about 80°C in a boiling-reflux condenser for 2 h and finally filtered with a vacuum flask and dried at 103°C for about 24 h [9].

Thermal analysis

The TG-DTG analyses were performed on a DuPont 9900 Thermal Analysis System (DuPont Co., USA). The samples after impregnation were subjected to heat under a controlled atmosphere of nitrogen (60 ml min^{-1}) from room temperature (25°C) up to 1.000°C at a constant heating rate of 5 and 10°C min^{-1}. All the samples were crushed with a pestle and a mass of ~10 mg was used. Prior to the experiments, calibrations for the thermal instrument were performed using the standards provided by the DuPont Co. The SEM analysis was carried out on the HITACHI S-2400 (Hitachi Co., Japan). The surface of the impregnated sample as well as the activated carbon thus ground was coated with a thin, electric conductive gold film. The excitation voltage used was 20 kV.

Results and discussion

Thermal behavior

The TG data of the corn cob unimpregnated with $ZnCl_2$ essentially reveal a multi-stage thermochemical decomposition process, as shown in Fig. 1. The mass loss of sample between 200 and 220°C is mostly due to the dehydration processes, which are associated with the existence of various structures and forms of water bonding [15]. It should be noted that the measurement of the moisture content of the sample was carried out at 105°C. The volatile products from the sample of corn cob are evolved at temperatures higher than 220°C. It is well known that the thermochemical processes include parallel and competitive reactions due to the heterogeneity in chemical composition of the sample studied [16]. The variety of the bonding of the volatile components is confirmed by the differences in the rates of thermal degradation. The maxima of the mass loss rate of sample (r_A), as shown in the DTG curve (Fig. 1), appear in the temperature range of 250–350°C. This observation is in agreement with the results of other studies on corn cob and samples with similar composition [4, 15]. Slight change of the mass loss of sample was observed in the range of 350–1000°C. The DTG data indicate that the values of r_A are small and decrease gradually, which are attributed to the presence of the carbonized products in the sample. Similar results are also obtained in another TG analysis of corn cob at a heating rate of 5°C min^{-1}.

The representative TG-DTG curves of corn cob samples impregnated with $ZnCl_2$ with various ratios (i.e., with the ratio of $ZnCl_2$ to corn cob of 20–200%, denoted as R_i) under heating rate of 10°C min^{-1}, are presented in the typical Fig. 2 for R_i=175%. The DTG results indicate that the major thermochemical decompositions

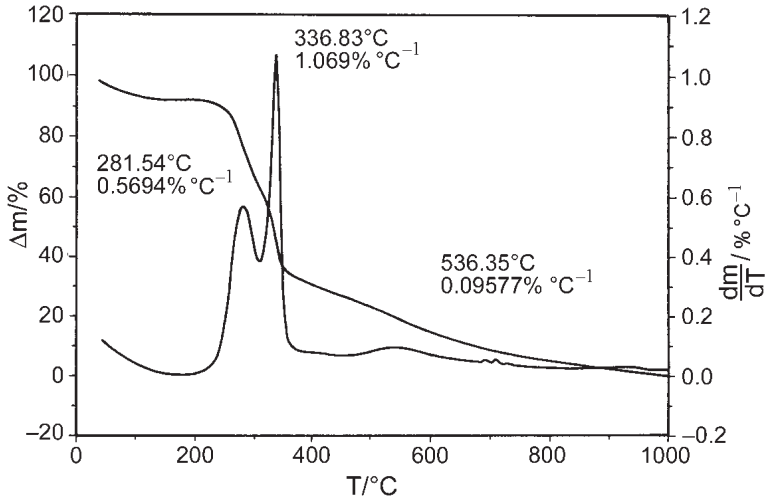

Fig. 1 TG-DTG curves of corn cob unimpregnated with $ZnCl_2$ under heating rate of 10°C min^{-1}

take place in the temperature ranges of 150–230 and 400–600°C. The mass loss rates display two peaks at about 180 and 500°C (Fig. 2). The occurrence of the first peak in the temperature range of 150 – 230°C can be attributed to the dehydration of the lignocellulosic material, the presence of unstable cellulosic fragments and the depolymerization of cellulose. The magnitude of the second peak in the temperature range of 400–600°C is qualitatively significant for the case with higher R_i. For example, the values of r_A, based on the DTG analyses, are 0.08 (at 531°C), 0.11 (at 462°C), 0.27 (at 496°C) and 0.32 % $°C^{-1}$ (at 499°C) for R_i= 50, 100, 150 and 175%, respectively. This is consistent with the BET surface areas (i.e., 960, 1114 and 1410 m^2 g^{-1} for R_i=100%, 150 and 175%, respectively) of the resulting activated carbons obtained from the previous study [5, 9]. A comparison of Fig. 2 with Fig. 1 indicates that the temperature ranges of the appearance of the second peak of impregnated samples are higher than those of unimpregnated samples (i.e., 400–600°C *vs.* 250–350°C). The peak occurs at about 500°C is probably associated with the active pyrolysis of the cellulosic fragments and the condensation processes which result in an increased content of aromatic clusters [15]. These suggested mechanisms indicate that $ZnCl_2$, which is a Lewis acid, promotes the aromatic condensation reactions and thus catalyzes the oxidation reactions at that temperature [14].

Concerning the thermal volatilization of $ZnCl_2$ it is due to its physical properties (i.e., melting point of 283–290°C and boiling point of 732°C). The Zn content of the corn cob samples impregnated with $ZnCl_2$ was determined by acid digestion and analysis of the solution using the inductively coupled plasma-atomic emission spectrometer (JARREL-ASH Co., model ICAP 9000). The results of the Zn analysis are 12, 30800, 52900 and 95200 μg g^{-1} for some samples with R_i=0, 20, 50 and 100%, re-

spectively. It was reported that some reactions of $ZnCl_2$ with an oxygen donor (e.g. water) could be occurred by hydrolysis into ZnO and subsequent immobilization with silica to silicate or aluminate compound [17]. Also, it may be reasonable to speculate that the amounts of evaporated Zn could be limited by physical trap into porous structure of the resulting activated carbon during the TG analysis of the corn cob/$ZnCl_2$ samples [17]. They suggested that maximum rate of $ZnCl_2$ evaporation could occur in the temperature ranges of 400–600°C, but at this stage some aromatic condensation reactions also take place among the adjacent molecules, which result in the evolution of gaseous products (e.g. H_2 and CO) from the hydroaromatic structure of the precursor. Further studies on the Zn mass balance and gaseous product analysis in the experimental processes would be helpful.

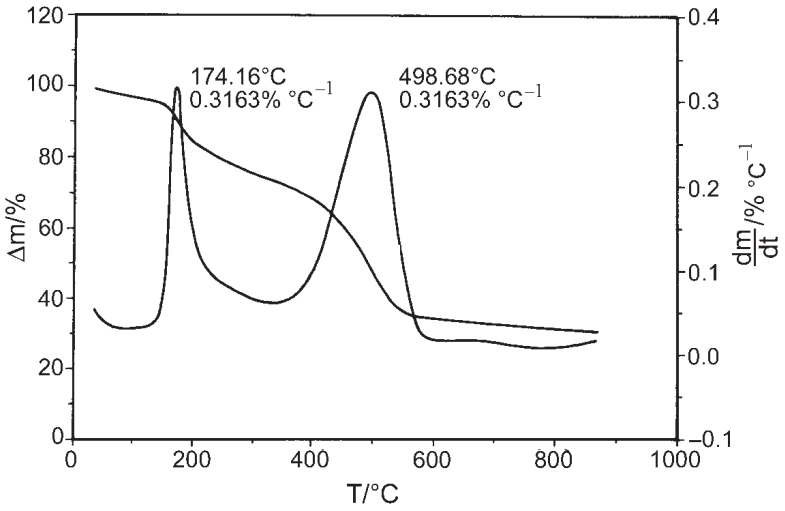

Fig. 2 TG-DTG curves of corn cob impregnated with $ZnCl_2$ with ratio of 175% under heating rate of 10°C min^{-1}

SEM observation

The porous structure examination of the samples can be clearly seen from the SEM photographs. From Fig. 3, it can be seen that the original material, corn cob impregnated with $ZnCl_2$ with R_i of 175 % does not have a well defined pore structure but displays cellular and corrugated textures. However, the pores can be developed and further enhanced by the chemical activation during the course of pyrolysis, which results in the formation of some pores as illustrated in Fig. 4. With the increase of impregnation ratio from 100 to 175%, more pores appear in the interporous areas (Fig. 4(a) *vs.* Fig. 4(b)). This difference in the development of pore structure can also exhibit the apparently larger BET surface area (i.e., 960 *vs.* 1410 $m^2 g^{-1}$ with R_i of 100 and 175%, respectively) of the resulting activated carbons produced with higher impregnation ratio of $ZnCl_2$ described previously [5, 9].

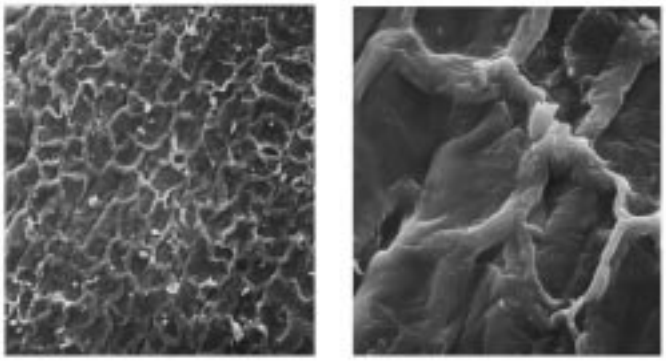

Fig. 3 SEM photographs of corn cob impregnated with $ZnCl_2$ with ratio of 175% $ZnCl_2$ (left: ×400; right: ×2000)

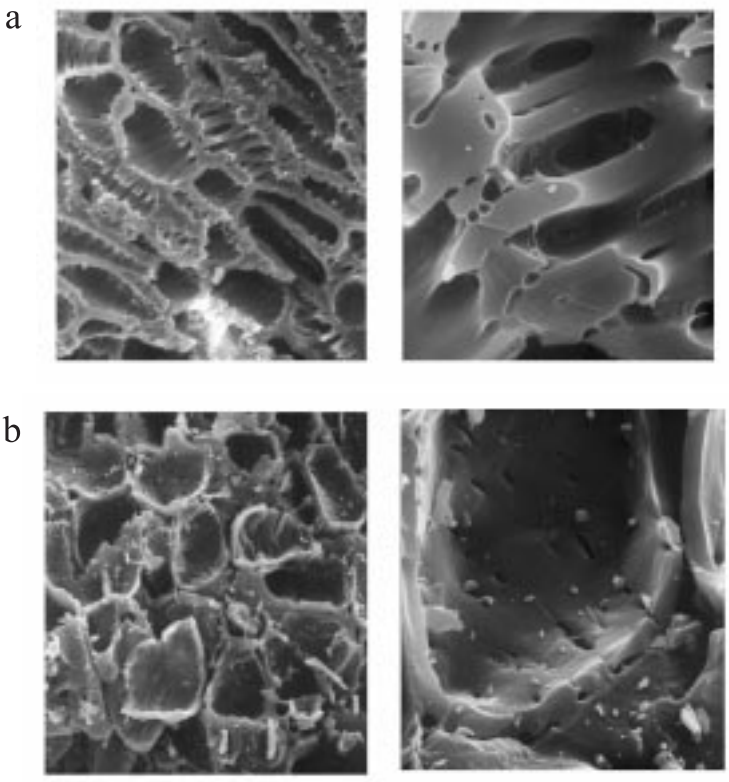

Fig. 4 SEM photographs of the resulting activated carbon produced previously [5, 9] by chemical activation with $ZnCl_2$ impregnation ratio of a – 100% and b – 175% under pyrolysis temperature of 500°C (with pre-pyrolytic heating rate of 10°C min^{-1}) and soaking time of 0.5 h (left: ×400; right: ×2000)

Conclusions

The TG analysis was used to investigate the thermochemical decomposition of the agricultural waste corn cob impregnated with chemical activator of $ZnCl_2$, as a precursor material for the preparation of activated carbon. It is established that the major changes in the thermochemical variations of mass occur in two temperature intervals, i.e., 150–230 and 400–600°C. The proper decomposition processes can reasonably explain these results. It is notably found that the peak occurred at about 500°C from the DTG curve is highly consistent with the previous results which indicated the optimal pyrolysis temperature of 500°C with similar experimental conditions for producing activated carbons. From the results of the present study, it was suggested that the data of the thermal analysis of TG-DTG seem to be used as an instrumental technique for a preliminary study on finding the optimal operating parameters, including pyrolysis temperature. The development of the pore structure of the resulting activated carbons thus obtained previously was also examined and explained using the scanning electron microscopy (SEM). Also, further studies on the estimates of the kinetic constants associated with the degradation of unimpregnated and impregnated corn cob samples will be made and these data would be useful for pyrolysis reactor design.

* * *

We sincerely thank the National Science Council, Taiwan, for the financial support (under Grant NSC 85-2211-E-041-002) of this project.

References

1 M. O. Bagby and E. W. Widstrom, Corn: Chemistry and Technology (Eds: S. A. Watson and P. E. Ramstand), Amer. Assoc. of Cereal Chemists, St. Paul (USA) 1987, p. 575.
2 N. Butuk and R. V. Morey, Trans. ASAE, 30 (1987) 543.
3 N. I. Perotti and O. E. Molina, Biol. Wastes, 26 (1988) 125.
4 P. Aggarwal and D. Dollimore, J. Thermal Anal., 50 (1997) 525.
5 W. T. Tsai, C. Y. Chang and S. L. Lee, Carbon, 35 (1997) 1198.
6 S. S. Yang, C. B. Wei, K. Koo and S. S. Tsai, J. Biomass Energy Soc. Chin. (Taiwan), 10 (1991) 70 (in Chinese).
7 R. C. Bansal, D. B. Donnet and H. F. Stoekli, Active Carbon, Marcel Dekker, New York 1988, p. 4.
8 J. M. Ebeling and B. M. Jenkins, Trans. ASAE, 28 (1985) 898.
9 W. T. Tsai, C. Y. Chang and S. L. Lee, Bioresource Technol., 64 (1998) 211.
10 C. J. Kirubakaran, K. Krishnaiah and S. K. Seshadri, Ind. Eng. Chem. Res., 30 (1991) 2411.
11 F. Caturla, M. Molina-Sabio and F. Rodriguez-Reinoso, Carbon, 29 (1991) 999.
12 A. Ahmadpour and D. D. Do, Carbon, 34 (1996) 471.
13 A. Ahmadpour and D. D. Do, Carbon, 35 (1997) 1723.
14 W. Heschel and E. Klose, Fuel, 74 (1995) 1786.
15 N. Shopova, V. Minkova and K. Markova, J. Thermal Anal., 48 (1997) 309.
16 R. K. Agrawal, Can. J. Chem. Eng., 66 (1988) 403.
17 S. Stucki and A. Jakob, Waste Manag., 17 (1997) 231.