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Activated carbons from plum stones

AGATA PAWLICKA, BEATA DOCZEKALSKA, MONIKA BARTKOWIAK,
MONIKA JANECKA
Institute of Chemical Wood Technology, Department of Wood Technology, Poznan University of Life Sciences

Abstract: *Activated carbons from plum stones.* The aim of this paper was to obtain a series of activated carbons (ACs) by chemical activation of greengage plum stones and to determine content of surface oxygen groups. Thermoanalytical methods also were applied in investigation. Precursor was pyrolysed at the temperature of 600°C, 700°C and 800°C. Carbonizates were activated with sodium and potassium hydroxide at a temperature about 150°C higher than the temperature of carbonization for 30 min. The type of hydroxide and temperature of activation process influence on the chemical properties and thermal stability of obtained activated carbons.

Keywords: greengage plum stones, activated carbon, chemical activation, TG, surface oxygen groups

INTRODUCTION:

The preparation of activated carbons (ACs) generally comprises two steps, the first is the carbonization of a raw material or precursor and the second is the carbon activation. The carbonization consists of a thermal decomposition of raw materials, eliminating non-carbon species and producing a fixed carbon mass with a rudimentary pore structure (very small and closed pores are created during this step). On the other hand, the purpose of activation is to enlarge the diameters of the small pores and to create new pores and it can be carried out by chemical or physical means. During chemical activation, carbonization and activation are accomplished in a single step by carrying out thermal decomposition of the raw material impregnated with certain chemical agents such as H_3PO_4, H_2SO_4, HNO_3, NaOH, KOH and $ZnCl_2$. Physical or thermal activation uses an oxidizing gas (CO_2, steam, air, etc.) for the activation of carbons after carbonization, in the temperature range from 800 to 1100ºC. The carbonization can be carried out using tubular furnaces, reactors, muffle furnace and, more recently, in glass reactor placed in a modified microwave oven (Hernandez-Montoya et al. 2012).

In view of the above, the aim of this paper was to obtain a series of activated carbons by chemical activation of greengage plum stones. Determination of surface oxygen functional groups and application of thermogravimetric analysis for activated carbons were described.

MATERIAL AND METHODS

Sample preparation: The greengage plum stones were cleaned with distilled water and dried at 105°C for 24 h. Next step was grounding of plum stones in roller mill, sieving and manually select only shells of stones. The crushed material was subjected to pyrolysis and carbonization. Processes have been carried out in a chamber reactor in oxygen free atmosphere by heating to 600°C, 700°C or 800°C at the temperature rate of 3°C/min and then, holding in stable conditions for 1 h. Carbonizates after grinding were activated with sodium and potassium hydroxide at mass ratio 1:4 in argon atmosphere at a temperature about 150°C higher than the temperature of carbonization for 30 min in nonporous ceramic reactor. ACs were extracted with 1% hydrochloric acid and then, with deionized water to the neutral pH.

Thermogravimetric analysis: The analysis of active carbons was carried out on a Labsys^{TM} thermobalance of the Setaram Company in the following conditions: final temperature - 1200°C, rate of temperature increase - 5 deg/min, atmosphere – helium flowing at the rate of about 2 dm^3/h.

Surface oxygen groups: Surface oxygen groups were determined according to the Boehm's method (Boehm 1994). A 0.25 g of each active carbon sample was placed in a 250 ml flask. After adding 25 ml of 0.1M solution of NaOH, $NaHCO_3$ and 0.05M solution of Na_2CO_3 (for determination of acidic groups) or 0.1M HCl (for determination of basic groups), the mixtures were shaked for 24 h. After filtering the mixtures, 10 ml of each filtrate was pipetted and the excess of base and acid was titrated (Tashiro indicator) by 0.1M solution of HCl or NaOH, respectively. All experiments were twice repeated. The numbers of acidic sites of various types were calculated under the assumption that NaOH neutralizes carboxyl, phenolic and lactonic; Na_2CO_3 – carboxyl and lactonic; and $NaHCO_3$ only carboxyl groups. The number of surface basic sites was calculated from the amount of HCl which reacted with carbon (Bandosz 1999).

RESULTS AND DISCUSSION:

Heteroatoms, such as oxygen, hydrogen or nitrogen have a strong influence on the mechanisms of the adsorption process. The most important from them is oxygen which is present in chemical groups: chromene and pyrone have Lewis base properties; anhydrides, lactones, lactols, carboxyls or phenols have acidic character (Benaddi et al. 2000). Understanding physical and chemical properties of the surface of carbonaceous materials requires a use of several methods of direct analysis (eg. acid-base). In this work the chemical structure of the surface of activated carbons was determined by using acid-base method (Pawlicka et al. 2013). Thermogravimetry (TG) is a technique for measuring of weight loss of samples as a function of temperature or time and is often used to study the thermostability of organic and inorganic compounds. This technique is also used to investigate surface and adsorption properties of porous materials (Pawlicka el al. 2013).

According to the data concerning the content of surface oxygen groups obtained to the Boehm's method (table 1), shows that two received activated carbons contain practically zero lactonic and phenolic groups. In samples from hornbeam wood there was not detected the content of carboxyl groups. The greatest amount of carboxyl groups showed activated carbon prepared in activation process at the 850°C with sodium hydroxide. In the case of sodium hydroxide activation when temperatures of activation processes are increasing, the total surface acidity of ACs is decreasing but alkalinity increase. The activated carbons formed during the activation process with potassium hydroxide in highest temperature showed more acidic than basic character of surface. Content of basic and acidic groups for KOH-activated carbons is quite high.

Table 1. Surface oxygen functional groups – acidic and basic properties for activation time 30 min

Activated carbon	Functional groups [mmol/g]				
	Acidic			Acidic (total)	Basic (total)
	carboxyl	lactonic	phenolic		
750/NaOH	0.10	0.15	0.50	0.75	0.40
850/NaOH	0.50	x	x	0.50	0.80
950/NaOH	0.10	x	x	0.10	1.44
750/KOH	0.15	0.10	0.75	1.00	1.20
850/KOH	0.15	0.05	0.25	0.45	0.80
950/KOH	0.10	0.25	0.25	0.60	0.45

Weight loss determined for each active carbons are presented in Table 2. Lowest weight loss was obtained for KOH-activated carbons in activation process at 850°C and amounted 12.05% . For NaOH-activated carbons lowest weight loss was 17.69% and it was noticed at activation process at 750°C. In addition, in the case of ACs prepared with using potassium hydroxide increasing temperature of activation processes mostly decreasing weight loss.

Table 2. Weight loss of activated carbons determined by thermogravimetric

Sample	Weight loss [%]		
	20-150°C	200-1200°C	Total
750/NaOH	0.35	17.15	17.69
850/NaOH	0.48	18.15	18.90
950/NaOH	0.40	17.95	18.61
750/KOH	1.40	14.35	16.06
850/KOH	0.72	11.44	12.05
950/KOH	0.45	11.47	12.14

Figures 1 and 2 presents thermograms of activated carbons from greengage plum stones. It was found that the products obtained using sodium hydroxide as activator are more thermal stable than activates prepared with using potassium hydroxide. For both activators in the range 600°C - 900°C it has been observed decomposition of surface oxygen functional groups. As can be seen in DTG curves of KOH-activated carbons are different from DTG curves of NaOH-activated carbons, what shows differences in surface characteristics of studied carbons. Result shows that on the surface of carbons were created oxygen functional groups with varying thermal stability.

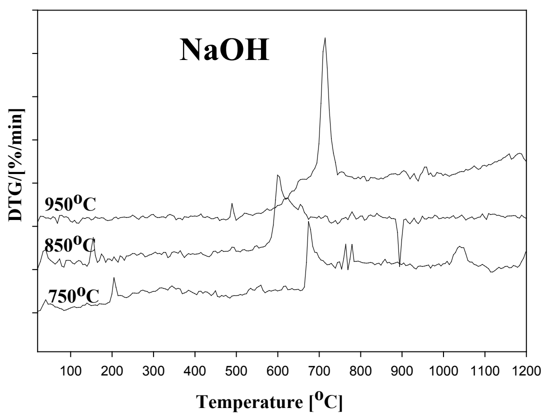

Fig. 1. DTG curves of ACs from greengage plum stones activated with sodium hydroxide in 30 min

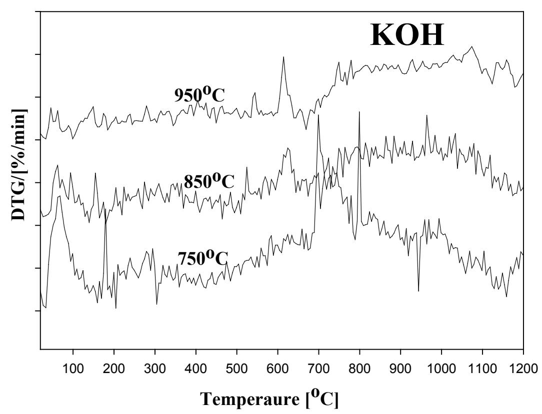

Fig. 2. DTG curves of ACs from greengage plum stones activated with potassium hydroxide in 30 min

Samples have been named according to the following scheme - 750/NaOH or 750/KOH, where 750 means temperature of activation and NaOH or KOH mean type of used activator.

CONCLUSIONS

Results of our investigations concluded that:

1. The type of used hydroxide influence on the chemical surface properties of ACs. Application of KOH conduces formation of acid groups when NaOH-activated carbons showed presence of basic nature groups.
2. The results of thermogravimetric studies indicate that the type of hydroxide influence the formation on the surface of carbons oxygen functional groups with varying thermal stability. KOH-activated carbons are the most thermal stable after activation at temperature 850°C and 950°C.

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Streszczenie: *Węgle aktywne z pestek śliwy.* W pracy otrzymano węgle aktywne z łupin pestek śliwy renklody. Procesy karbonizacji prowadzono do temperatury końcowej 600^{o}C, 700^{o}C oraz 800^{o}C. Karbonizaty aktywowano przy udziale wodorotlenku sodu lub wodorotlenku potasu w czasie 30 minut, w temperaturze o 150^{o}C wyższej niż temperatura karbonizacji.
Do analizy otrzymanych materiałów węglowych wykorzystano termograwimetryczne techniki pomiaru i określono procentowe ubytki masy w funkcji temperatury. Metodą Boehma określono zawartość powierzchniowych tlenowych grup funkcyjnych. Stwierdzono, że rodzaj zastosowanego wodorotlenku wpływa na chemiczny charakter powierzchni otrzymanych węgli aktywnych oraz na tworzenie się na powierzchni węgli tlenowych grup funkcyjnych o zróżnicowanej odporności termicznej.

Corresponding authors:

Agata Pawlicka*, Beata Doczekalska, Monika Bartkowiak, Monika Janecka
Institute of Chemical Wood Technology
Poznan University of Life Sciences
ul. Wojska Polskiego 38/42
60-637 Poznań
Poland
*e-mail: apawlicka.wtd@o2.pl