Annals of Warsaw University of Life Sciences - SGGW
Forestry and Wood Technology № 92, 2015: 88-91
(Ann. WULS - SGGW, For. and Wood Technol. 92, 2015)

Activated carbons from plant materials

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Abstract: *Activated carbons from plant materials.* The aim of this paper was to obtain a series of active carbons from different plant materials and to determine content of surface oxygen groups. Plant materials to be tested: rapeseed straw, flax and hemp shives, willow and miscanthus. A technology of obtaining active carbons from lignocellulosic precursors by chemical activation with NaOH was described. The precursors were pyrolysed at the temperature of 600°C and 700°C. Carbonizates were activated with potassium hydroxide at a temperature about 150°C higher than the temperature of carbonization in nonporous ceramic reactor. The type of material and temperature of activation process influence on the chemical surface nature of activated carbons.

Keywords: activated carbons, surface oxygen functional groups, Boehm's titration method

INTRODUCTION:

Almost all materials containing elementary carbon in organic compounds can be used as precursors for the production of activated carbons. However, they should exhibit the highest content of elementary carbon, low content of volatile and organic substances, high mechanical and thermal resistance, also be cheap and easily available. For these reasons, fossil carbons, peat, wood and coconut shells are used nowadays for the industrial production of activated carbon precursors. An alternative solution could be the use of other, nonconventional lignicellulosic materials. Due to a large number of naturally available cellulose-lignin composites, it would be possible to obtain ACs with different structures and properties. The uniqueness of lignocellulosic materials comes from diversified chemical and structural composition of the plant tissue, both in ultramicro and supermicro scale (Pelaez-Cid and Teutli-Leon 2012). Their advantages also include availability, renewability and large supplies of the resources, low price and environmental biocompatibility.

Surface chemistry activated carbons significantly influences the wettability, adsorptive, electrical, electrochemical, catalytic, acid–base, redox, hydrophilic–hydrophobic, and other properties. The surface oxygen functional groups can be classified into three classes according to their chemical properties: acidic, basic, neutral. Functional groups such as carboxylic acid or carboxylic anhydride, lactone, and phenolic hydroxyl have been postulated as the sources of surface acidity (Boehm 2002). Basicity of activated carbon can be associated with: (i) resonating-electrons of carbon aromatic rings that attract protons, and (ii) basic surface functionalities (e.g., nitrogen containing groups) that are capable of binding with protons. It was pro-posed that certain oxygen containing surface functionalities such as chromene, ketone, and pyrone can contribute to the carbon basicity (Montes-Moran et al. 2004). Surface oxygen groups on carbon materials are usually determined by titrations in aqueous solutions. One of the standard methods is the Boehm method (Pawlicka and Doczekalska 2013). Additionally, temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), or methods involving diffuse reflectance FTIR (DRIFTS) can also be used (Zhou et al. 2007).

In the present study, the Boehm titration method was employed for the determination of oxygen groups on the surface of different carbon materials prepared from plant materials. Plant materials to be tested: rapeseed straw, flax and hemp shives, willow and miscanthus.

MATERIAL AND METHODS:

Plant materials: Rapeseed straw, flax and hemp shives and miscanthus were obtained from experimental field of the Institute of Plant Genetics, Polish Academy of Sciences. *Salix viminalis* came from experimental cultivation of the Poznan University of Life Sciences.

Sample preparation: Lignocellulosic materials were cleaned with distilled water and dried at 105°C for 24 h. The crushed plant materials were subjected to pyrolysis and carbonization. These processes have been carried out in a chamber reactor in oxygen free atmosphere by heating to 600°C, 700°C at the temperature rate of 3°C/min and then, holding in stable conditions for 1 h. Carbonizates after grinding were activated with 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. Activated carbons (ACs) were extracted with 1% hydrochloric acid and then, with deionized water to the neutral pH.

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

According to the data concerning the content of surface oxygen groups obtained to the Boehm's method (table 1), shows that the seven of the ten received activated carbons contain carboxyl groups. The greatest amount of carboxyl groups showed activated carbon prepared from flax shives at the temperature 750°C. Lactone groups content are lower and amounts 0.05-0.20 mmol/g. In turn, the amount of phenol groups is much higher. When temperatures of activation processes are increasing, the total surface acidity of carbons from lignocellulosic materials is decreasing. Carrying out the activation process at 850°C will block the formation of surface acidic groups.

The activated carbons obtained from rapeseed straw, hemp shives and flax shives showed basic character of the surface while ACs from salix wood and miscanthus showed acidic character of the surface.

Microporous properties of activated carbons depend not only on the experimental conditions of the carbonization and activation steps but also preponderantly on the original nature and structure of the involved precursor. The type of lignocellulosic precursor, and activation temperature have an effect on the chemical structure of the surface active carbons.

Table 1. Surface oxygen functional groups

Acitve carbon	Functional groups [mmol/g]				
	Acidic			Acidic (total)	Basic (total)
	carboxyl	lactonic	phenolic		
S/750	0.19	0.01	0.97	1.17	0.39
S/850	x	0.20	0.58	0.78	0.58
R/750	0.20	x	0.87	1.07	3.33
R/850	x	x	0.59	0.59	3.17
M/750	0.20	0.10	0.88	1.18	0.44
M/750	x	0.10	0.59	0.69	0.55
H/750	0.20	0.20	0.79	1.19	1.29
H/850	0.1	x	0.80	0.90	1.37
F/750	0.24	0.05	0.93	1.22	1.37
F/850	0.10	0.10	0.49	0.69	1.10

x - below the method detection limit

Samples have been named according to the following scheme - S/750 or H/850, where "S" means Salix viminalis wood, "R" rapeseed straw, "M" miscanthus, "H" hemp shives and "F" flax shives. Next numbers present temperature of activation.

CONCLUSIONS

Results of our investigations concluded that:

1. The increase of the activation temperature reduces content of acid groups of active carbons. Carrying out the activation process at 850°C will block the formation of surface acidic groups.
2. Activated carbons from rapeseed straw, hemp shives and flax shives are showing higher surface alkalinity.
3. Activated carbons from salix wood and miscanthus showed acidic character of the surface.

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Streszczenie: *Węgle aktywne z surowców roślinnych.* W pracy otrzymano węgle aktywne z wierzby *Salix viminalis*, miskantusa, słomy rzepakowej oraz paździerzy lnianych i konopnych poprzez pirolizę i karbonizację w temperaturach 600°C lub 700°C. Następnie karbonizaty aktywowano za pomocą wodorotlenku potasu w temperaturze o 150°C wyższej niż temperatura karbonizacji. Oznaczono zawartość powierzchniowych grup tlenowych metodą Boehma. Stwierdzono, że rodzaj zastosowanego prekursora lignocelulozowego i temperatura aktywacji mają wpływ na chemiczny charakter powierzchni otrzymanych węgli. Węgle aktywne otrzymane ze słomy rzepakowej, paździerzy lnianych i konopnych wykazują zasadowy charakter powierzchni, a węgle aktywne z wierzby i miskantusa kwasowy charakter powierzchni.

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