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Synthesis of nanoporous carbon from plant wastes and coal treatment products

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Synthetic nanoporous carbons are produced from mixtures containing coal tar pitch and furfural in different proportions. It was determined that the surface area and amount of oxygen containing groups on the surface significantly depend on the composition of the initial mixture. Best quality carbon with developed pore structure with prevailing content of micropores was obtained from the precursor containing 50% furfural. Various oxygen containing structures are established on the synthetic nanoporous carbon surface.

Key words: nanoporous carbon, synthesis, treatment products, plant, coal.

INTRODUCTION

Considerable amount of liquid products is separated during the different thermal treatments (pyrolysis, gasification, *etc*.) of plant wastes and coals, but efficient exploitation of these liquid products has not been found yet. Therefore there is a need to promote the development of successful solution for their effective utilization. Thus liquid products from pyrolysis of agricultural wastes and low rank coals can be used for the fabrication of monolithic carbon as a precursor for the production of porous carbon. When produced on the base of pyrolysis liquid products, microporous carbons are practically ash free carbons. By using a combination of sources and appropriate methods of treatment, porous carbons with different chemical surface properties could be obtained. Synthetic carbons with various surface chemistry can be obtained by pyrolysis of raw materials containing heteroatoms in different forms or pyrolysis of raw material in the presence of heteroatoam-containing substances [1–3]. Other possibility is modification of the carbon surface with heteroatom-containing reagents [4–6].

Investigations are intended to obtain nanoporous carbons with different chemical character of the surface from mixtures of coal tar pitch and biomass treatment products – this could reveal the possibility for effective utilization of pyrolysis liquid products by production of synthetic carbons with wide application area.

The aim of our investigations is the invention and development of process for production of nanoporous carbons with different chemical character of the surface on the base of coal and plant treatment products. Present work deals with the investigation of the influence of the proportion of the initial mixture from coal tar pitch and furfural on the properties of produced nanoporous carbons.

EXPERIMENTAL

Synthesis procedure

Coal tar pitch with softening point 72°C was heated up to 140°C until melting and furfural was added. The obtained mixtures was treated with conc. H_2SO_4 with continuously stirring until solidification. The solid product obtained was heated up to 600°C in a covered silica crucible with a heating rate of 10°C/min under nitrogen atmosphere (carbonization process). Steam activation with water vapour at 800°C for 1 h of obtained carbonizates was used for nanoporous carbon producing.

Porous carbon characterization

The porous structure of carbon adsorbents was studied by N_2 adsorption at 77 K. The total pore volume (V_{total}) is derived from the amount of N_2 adsorbed at a relative pressure of 0.95, assuming that the pores are then filled with liquid adsorbate. The Dubinin-Radushkevich equation was used to calculate the micropore volume (V_{micro}) [7]. The mesopore volume was calculated by subtracting the amount adsorbed at a relative pressure of 0.1 from that at a relative pressure of 0.95.

Oxygen-containing functional groups.

The amount of oxygen-containing functional groups with increasing acidity was determined by Boehm's method of titration with basic solutions of

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different base strength ($NaHCO_3$, Na_2CO_3, NaOH, C_2H_5ONa). For this purpose the samples were agitated for at least 16 h with 0.05 N solutions of the four bases. The amount of Na^+ ions remaining in the solution is determined by adding an excess of standard HCl and backtitrating [8]. The basic groups content of the oxidized samples is determined with 0.05 N HCl [9].

pH determination

The procedure is as follows: 4.0 g of carbon (ground, undried) is weighed into a 250 ml beaker and 100 ml of water is added. The beaker is covered with a watch glass and heated to boiling temperature for 5 minutes. The mixture is set aside and the supernatant liquid is poured off at 60°C. The decanted portion is cooled down to room temperature and is measured to nearest 0.01 pH.

RESULTS AND DISCUSSION

For the production of synthetic nanoporous carbon, 100 g of the mixture of pitch obtained from apricot stones steam pyrolysis tar and furfural in the proportion 70:30, 60:40, 50:50 and 40:60.

The characterization of initial pitch (Table 1) is valuable for understanding the processes taking place during the preparation and modification of the precursor mixture with H_2SO_4.

Table 1. Elemental analysis of coal tar pitch.

Samle	Softening point, °C	Elemental analysis (daf), %					
		C	H	N	S	O (diff.)	C/H
Pitch initial	72	90.90	4.95	0.90	0.50	2.75	1.53

daf – dry and ash free basis.

Data show, that pitch precursor possess middle value of softening point temperature. The amount of oxygen containing structures is not high. C/H ratio indicates mainly presence of aromatic structures in the pitch.

Content of neutral parts, bases, acids and phenols in the pitch precursor was determined by the following scheme (Fig. 1).

Obtained results are presented in Table 2. Data in Table 2 show, that precursor pitch contains predominantly neutral compounds. The presence of small amounts of phenols, acids and relatively higher amount of organic basis is determined. The results indicate that small quantity of structures can be involved in condensed reaction with formation of higher molecular products to produce solid product. This fact determines the necessity for adding reactive structures to the pitch what will allow easier solidification of the precursor. We used furfural as reactive structure.

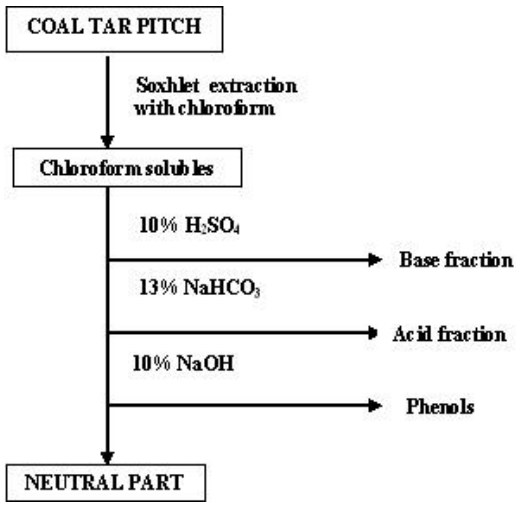

Fig. 1. Scheme for the separation of pitch.

Table 2. Content of neutral parts, bases, acids and phenols in the pitch precursor.

Samples	Solubility class separation of CHS* part of pitches, %			
	Neutral part	Phenols	Bases	Acids
Pitch initial	86.68	2.57	9.16	1.59

* - CHS - chloroform soluble.

We decided to use as a precursor mixture of coal tar pitch and furfural, because the last is inclined to polymerization reactions and will promote solidification of the mixture. The mixtures containing different amounts of furfural were used. The proximate and elemental analysis of obtained carbons is presented in Table 3. Data show, that with decreasing the content of furfural in the initial mixture increase the content of carbon in the final product due to the prevailing content of aromatic structures in the pitch. As the furfural inserts oxygen in the precursor, higher amount of furfural increases the content of oxygen in the synthesized carbon and make it more alkaline. Pitch contains mineral compounds and introduces them in the precursor and respectively in the final product.

Table 3. Chemical composition of the carbon adsorbents obtained from mixtures of biomass products.

Sample	Proximate analysis, %			Elemental analysis (daf), %				
	W	Ash^d	pH	C	H	N	S	$O_{diff.}$
S_{60}	5.8	0.61	8.4	80.27	2.31	0.31	0.29	16.82
S_{50}	5.1	0.72	7.5	81.14	2.56	0.28	0.54	15.48
S_{40}	5.5	0.82	7.5	82.16	2.66	0.30	0.66	14.22
S_{30}	5.2	0.93	7.3	82.87	2.71	0.32	0.71	13.39

daf – dry and ash free basis; d – dry basis; W – water content.

It is known that the value of iodine number is close to surface area of sample determined by N2 adsorption [10]. That is why the iodine number was used as preliminary test for surface area of S60, S50, S40, S30 – carbons obtained from mixtures containing 60, 50, 40, 30% furfural obtained synthetic carbons.

Table 4 present the iodine numbers of the carbons obtained from mixtures of coal tar pitch with furfural in different proportions using the same conditions (activation temperature 800°C, duration of activation 1 h). The results confirm that there are significant differences in the surface areas of the obtained carbons. With the increase of the amount of furfural in the mixture the surface area of obtained carbon also increases. Data indicate that texture of this carbon is not too firm, but it is more reactive and this allows the formation of higher surface area in the result of interaction with activation reagent. This is confirmed from the decrease of the yield of the final product with the rising the content of furfural in initial mixture.

Table 4. Data for the adsorption of iodine on the surface of synthetic carbons, obtained from mixtures containing coal tar pitch and furfural in different proportion.

Parameter	Synthetic carbons			
	S_{60}	S_{50}	S_{40}	S_{30}
Iodine number, mg/g	1210	1100	900	750
Yield of nanoporous carbon, %	40	49	55	62

In addition to pore structure and surface area, other important characteristic of obtained carbon is the surface chemistry. Table 5 show the determined content of oxygen containing groups with acidic and basic character on the surface of obtained carbons.

The increased content of acidic oxygen groups in the sample with higher content of furfural unambiguously indicates that inserting of oxygen in the precursor by furfural increases the formation of oxygen containing structures in the final product, particularly the acidic surface oxides. The amount of basic oxides does not depend significantly on the content of furfural in initial mixture.

Table 5. Acid-base neutralization capacities of the obtained carbons.

Sample	Base uptake, meq·g^{-1}				Acid uptake
	$NaHCO_3$	Na_2CO_3	NaOH	EtONa	HCl
S_{60}	0.043	0.092	0.293	1.386	0.592
S_{50}	0.024	0.053	0.138	0.977	0.585
S_{40}	0.019	0.034	0.081	0.739	0.575
S_{30}	0.012	0.023	0.049	0.599	0.555

More detailed characterization was performed with the sample obtained from mixture containing 50% furfural. The N_2 (77 K) adsorption isotherm of carbon obtained from mixture furfural:pitch – 50:50 is presented in Figure 2.

The adsorption investigations (steep increase in the beginning of the isotherm) reveal that the activation with water vapour leads to the formation of microporous carbon.

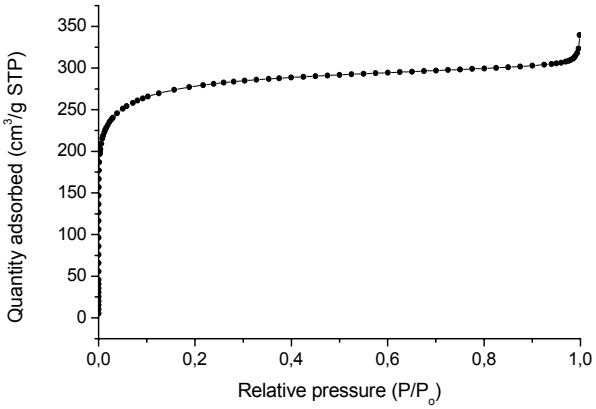

Fig. 2. N_2 (77 K) adsorption isotherm of synthetic carbon obtained from mixture containing 50% furfural.

The surface area and volumes of micro-, meso- and macropores of the carbons are presented in Table 6. Data show prevailing content of micropores in the obtained carbon and high surface area.

Table 6. Porosity characteristic of activated carbon obtained from mixture of biomass products.

Sample	N_2 BET surface area ($m^2 \cdot g^{-1}$)	Pore volume, ($cm^3 \cdot g^{-1}$)			
		Total	Micro	Meso	Macro
S_{50}	1100	0.492	0.236	0.138	0.118

The Pore size distribution of S_{50} sample is presented in Figure 3.

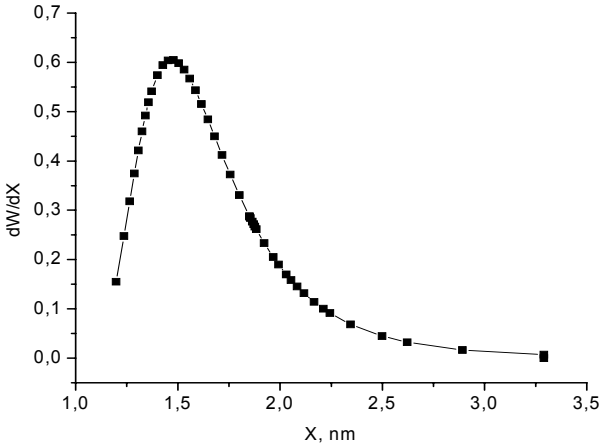

Fig. 3. Micropore size distribution of synthetic carbon obtained from mixture containing 50% furfural and 50% coal tar pitch.

Figure 3 show that carbon obtained from initial mixture containing 50% furfural possesses predominantly micropores with size from 1.2 to 2.0 nm. The

prevailing amount of pores is with size around 1.6 nm. This pore size distribution is appropriate for application of obtained carbon in many fields of industry because prevailing amount of pores are accessible for great number of organic and inorganic molecules.

CONCLUSIONS

It was determined that mixtures of furfural and coal tar pitch are appropriate raw material for synthesis of nanoporous carbon with insignificant ash content. The surface value and amount of oxygen containing groups on the surface significantly depend on the composition of the mixture. The activation is faster when carried out with carbon obtained from mixture with higher content of furfural. Considerably amount of oxygen structures is established on synthetic carbon surface. Best result was achieved using precursor containing 50% furfural. The obtained carbon possesses developed pore structure with prevailing content of micro-pores.

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СИНТЕЗ НА НАПОРОРЕСТ ВЪГЛЕН ОТ ПРОДУКТИ НА ПРЕРАБОТКА НА РАСТИТЕЛНИ ОТПАДЪЦИ И ВЪГЛИЩА

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(Резюме)

Синтетични нанопорести въглени са получени на основата на смеси, съдържащи каменовъглен пек и фурфурол в различно съотношение. Определено е, че специфичната повърхност и съдържанието на кислородни групи върху нея в значителна степен зависи от състава на изходната смес. Най-висококачествен въглен, с развита порьозна структура и преобладаващо съдържание на микропори, е получен от суровина, съдържаща 50% фурфурол. Кислородсъдържащи структури с различен характер са определени върху повърхността на получените синтетични нанопорести въглени.