

## ACTIVATED CARBON FOR GAS ADSORPTION

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### Abstract

The new technology of the cheap activated carbon production fabricated by the special thermal treatment of the impregnated raw (wood, sawdust, lignin, straw, paper for recycling, peat etc.) was developed. The use of specific organic and non-organic compounds as raw impregnates offers production activated carbons with controlled porous structure and high yield (up to 50 weight %)

Developed advanced technology allows to produce the homogeneous carbon adsorbents with benzene pore volume 0,3-0,6 cm<sup>3</sup>/g (70-80 % - micropores fraction), nitrogen surface area up to 1100 m<sup>2</sup>/g, iodine adsorption capacity 40-70 weight % and methane adsorption capacity up to 100 mg/g (3,5 MPa, 20°C). A thermo chemical decomposition process application was developed and discussed. Impregnated cellulose-containing raw for manufacture special activated carbon materials for methane storage systems with high micro porosity, surface area and narrow micropore size distribution was obtained. Simplicity and low power-consumption of the technology are the reason of a low cost of the activated carbon which is interesting for the market today.

### INTRODUCTION.

Advanced industry and science have a need for the carbon materials with special properties: high porosity and specific surface. One of goals of this paper is the development of a new method for direct regulation of the carbon materials chemical composition and structure from cellulose-containing raw. The method is based on the combustion treatment of wood impregnated by catalyst.

The wide scale of cheap and high effective solid sorption materials is required for the successful adsorption technology development. At present a good deal of efforts are undertaken in the research and design of the solid sorption refrigerators, air-conditioning systems and heat pumps [1, 2] and adsorption systems for natural gas storage [3, 4].

The activated carbon fiber is one of such perspective materials. It has good kinetic characteristics of adsorption-desorption processes and fine adsorption capacity for different refrigerants (ammonia, acetone, water) and gases (methane) [4, 5]. Unfortunately, the high cost of activated carbon fibers prevents to its commercialization. Therefore the problem of the new and cheap adsorbents development is a high-priority task.

As a rule, the activated carbon adsorbents are produced in two stages: by the carbonization of wood for producing the coal and its further activation by steam [6]. Often high cost of adsorbents limits its applying. To reduce the cost the process of the fast activated carbon production is developed. This method is welcomed for both stages: carbonization and activation are performed simultaneously.

### Experimental methods and apparatus

The wastes of the wood manufacture were applied as a raw material and the Lewis acids and some inorganic salts were used as an impregnate. Impregnation is realized in plastic bath (modules 15) during 12 hours. The mechanical press was used to remove the excess of impregnate by squeezing of wood raw.

Thermal decomposition of the impregnated wood was realized in original scheme reactor [7]. A raw material was loaded in the steel reservoir. The special type propane - butane burner was joined to this reservoir. The inner part of the burner was made from a ceramic material to realize a phenomena of a stationary combustion filtering waves and to convert it in the heat radiation. Temperature inside the reservoir was varied by the rate of gas flow and by the ratio of propane and butane of in the combustible mixture.

The activated carbon adsorption characteristics measurement was made by the usual gravimetric method (benzene, nitrogen) and by the combined volumetric-gravimetric technique realized in the installation for high pressure adsorption investigations, designed in Luikov Heat and Mass Transfer Institute (methane).

The first experiments have shown the impregnated wood heating rate can be increased up to 50<sup>0</sup>C/min without any essential reduce of activated carbon yield and its quality. A protective gaseous media was generated at propane-butane and volatile substances of a wood pyrolysis combustion. A protective envelope from inorganic additions was formed at the carbon and promotes a high activated carbon yield.

In the table I the characteristics of obtained activated carbons with temperature heat treatment (THT) 500-800<sup>0</sup>C are presented.

Table 1 Characteristics of the carbon sorbents

№ sample	Impregnate		THT*, °C	Yield of sorbent, mas. %	Ion-exchange capacity, mmol/g	Activity for benzene, g/g
	№ Catalyst	Additive reagents				
0	-		500			0.03
1	1		600	41.9	0.7	0.18
			700	31,8	0.9	0.19
2	2		600	37.4	0.4	0.08
			700	32.6	0.3	0.15
			800	24.2	0.6	0.16
3	3		600	41.0	0.8	0.22
			700	31.4	0.7	0.23
4	4		600	49.5	1.3	0.33
			700	46.9	1.0	0.52
5	2	A	600	34.6	0.5	0.21
		A	700	31.6	0.9	0.22
6	2	B	600	32.7	1.5	0.20
		B	700	30.3	1.1	0.25
7	2	C	600	30.5	2.0	0.23
		C	700	35.5	1.5	0.45

\*-temperature heat treatment (THT)

From this data analysis it is clear that the increasing of carbonization- activation of polymeric raw temperature causes the rising of the benzene adsorption capacity for the activated carbons. The optimal temperature of the carbon treating is around 700<sup>0</sup>C. The further temperature increasing up to 800<sup>0</sup>C result in reducing of the carbon yield. The depending on the impregnated benzene composition adsorption activity of activated carbons with THT 700-800<sup>0</sup>C are varied from 0.15 to 0.52 g/g.

The sharp rising at the initial part of benzene isotherms testify to the developed microporous structure. Further progress in the isotherms and the histeresis loops shape are the evidence of the small percentage of the meso pores volume presented in the activated carbon. Following the analysis of benzene vapor adsorption-

desorption experimental isotherms the samples of activated carbons belong to the fine-pored adsorbents such as H3 on classification IUPAC. In the table 2 characteristics of porous structure ( $V_s$ ,  $V_{mi}$ ,  $V_{me}$ ,  $V_{ma}$ ,  $V_{sum}$ ) and adsorption activity of the carbon sorbent obtained at THT 700°C are presented.

It should be noted that introducing carbonization catalysts into the raw saw dust leads to significant rising of the carbon residue yield as compared to that obtained from a non modified material.

The structural and chemical heterogeneity of the cellulose raw material causes nonuniform distribution of additives throughout its volume (the impregnates are concentrated mostly in the cellulose pores, capillaries, interfiber space and amorphous regions). This results in a nonuniform carbonization and formation of a developed macro porous space which is preserved by an excess pressure of the gas phase formed during the thermal treatment of the impregnates. In Fig. 1- 2 the developed activated carbon (sample 4) macro structure is shown.

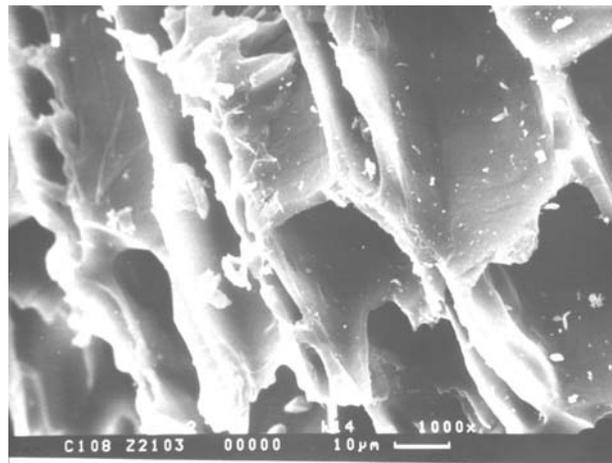
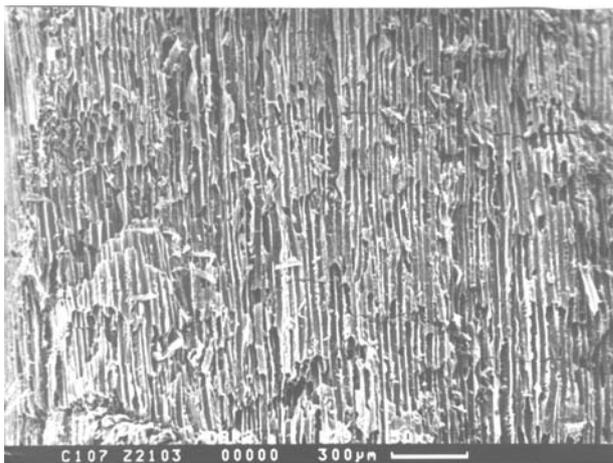


Fig 1. Active carbon element . Image multiplied by 30 times

Fig 2. Active carbon element . Image multiplied by 1000 times

Table 2.Characteristics of porous structure and adsorptive activity of carbon sorbents with temperature heat treatment 700°C

№ sample	Volume of adsorptive pores , cm <sup>3</sup> /g			$V_{mi}/V_s$	$V_{sum},$ cm <sup>3</sup> /g	$V_{ma},$ cm <sup>3</sup> /g	Activity for iodine, mas. %
	$V_s$	$V_{mi}$	$V_{me}$				
1	0.22	0.16	0.06	0.73	1.5	1.28	28
2	0.18	0.13	0.05	0.72	1.52	1.32	26
3	0.26	0.2	0.06	0.77	1.54	1.28	44
4	0.60	0.47	0.13	0.78	1.64	1.04	70
6	0.28	0.21	0.07	0.75	1.54	1.26	52
7	0.51	0.41	0.10	0.80	1.56	1.05	60

\* - № sample corresponds to index presented in table 1.

$V_s$  - bulk of adsorptive pores ( $V_s=V_{mi}+V_{me}$ ),  $V_{mi}$  - bulk micropores,  $V_{me}$  - bulk mezopores,  $V_{sum}$  - bulk of pores on moisture capacity,  $V_{ma}$  - bulk of macropores ( $V_{ma}= V_{sum}- V_s$ )

### Methane adsorption

Two samples of activated carbons obtained by the new technology were investigated as a methane sorption material. The surface area measured with “Micromeritics AccuSorb 2100” for the first sample 4 was 1040 m<sup>2</sup>/g and for the second one, sample 7 – 890 m<sup>2</sup>/g. The methane adsorption isotherms for this activated carbons at 293.15 K and at pressure up to 5 MPa are shown in Fig. 3. The Dubinin-

Radushkevich equation is used to describe entire adsorption isotherms with two terms and allows the interpolation of the experimental data:

$$a(P, T) = \left( \frac{W_o}{v_a} \right) \exp \left( -D T^2 \left[ \ln \left( \frac{P_a}{P} \right) \right]^2 \right) \quad (1)$$

$a(P, T)$  – adsorption capacity at temperature  $T$  and pressure  $P$ .

$P_a$  – internal pressure of adsorbed phase calculated by

$$P_a = \left[ \frac{T}{T_{cr}} \right]^2 P_{cr} \quad (2)$$

$v_a$  – molar volume of the adsorbate in the adsorbed phase: [8]:

$$v_a = v_b \exp(\Omega [T - T_b]) \quad (3)$$

$v_b$  – molar volume of the liquid adsorbate at the normal boiling point  $T_b$ ,  $\Omega = 0,0025 \text{ K}^{-1}$  - thermal expansion coefficient [9],  $T_{cr}$ ,  $P_{cr}$  – critical temperature and pressure.

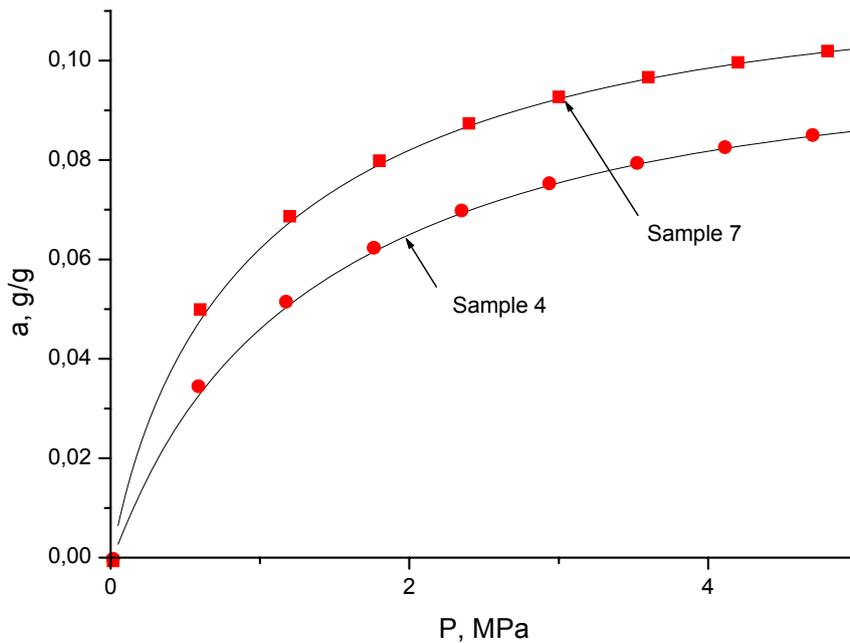


Fig. 3 Methane adsorption isotherms at 293 K. Experimental data – points; calculated data (Dubinin-Radushkevich equation) – lines

The empirical coefficients in Dubinin-Radushkevich equation were determined as  $W_o=0,3477$ ,  $D=1,421 \cdot 10^{-6}$  (sample 4) and  $W_o=0,4084$ ,  $D=1,135 \cdot 10^{-6}$  (sample 7).

Following Fig. 3 the lower surface area of adsorbed nitrogen and the lower adsorbed benzene pore volumes activated carbon sample 7 demonstrate the higher methane adsorption capacities than sample 4. The same anomalous phenomena have been observed by Jiang et al. [10] for methane adsorption in activated carbon AC610 (surface area  $486 \text{ m}^2/\text{g}$ ) and in activated carbon fibers KF1500 and A10 (surface area 1500 and  $1000 \text{ m}^2/\text{g}$  accordingly). Methane is a small size molecule gas and has low boiling point ( $-162^\circ\text{C}$ ), it could not be condensed inside the pores but only be adsorbed on the pore walls. Thus the pore size (optimal is  $11,4 \text{ \AA}$  [11]) is a critical factor for methane adsorption capacity. Apparently, the mean micropore size for sample 7 is greater than for sample 4 and so, in spite of

highest surface area, sample 4 adsorbed less methane molecules than sample 7. The lower coefficient  $D$  in Dubinin-Radushkevich equation for sample 7 is the evidence of its narrow micropore size distribution. It is the second factor that need to be accounted for methane adsorption isotherms in Fig 3 behavior.

## CONCLUSION.

One of the methods of direct regulation of the chemical composition and the structure of the carbon materials for obtaining its special properties is the decomposition of wood impregnated by catalysts of carbonization process. The carbon adsorbents with a high value of specific surface from up to 1100 m<sup>2</sup>/g, adsorptive pores volume from 0,18 to 0,6 cm<sup>3</sup>/g, methane adsorption capacity up to 100 mg/g (3,5 MPa, 20 °C) and the ion-exchange capacity from 1,1 to 2,0 mmol/g were developed.

The investigation of methane adsorption on the activated carbons has demonstrated that potential material for natural gas storage should have the following properties:

- High surface area
- Typical micropore diameter 11-12 Å
- Narrow micropore size distribution

Low cost activated carbons can be widely used for the purification and monitoring of the environment. Particularly, the designed activated carbons could be recommended as a filling agents for adsorbers of heat pumps and refrigerators, for natural gas storage systems and as a host material for chemical sorbents and catalysts.

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