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Adsorption of Volatile Aliphatic and Aromatic Hydrocarbons by Carbon Sorbents from Brown Coal and Hydrolytic Lignin

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Adsorption of volatile aliphatic and aromatic hydrocarbons by carbon sorbents from brown coal and hydrolytic lignin was studied. Carbon sorbents have been produced by pyrolysis and air-steam activation. Aliphatic hydrocarbons (pentane, hexane, heptane, octane) and aromatic hydrocarbons (benzol, toluol, o-xylol) were selected as for adsorptive investigations. At partial pressure below 10 kPa the sorbent from hydrolytic lignin has got the most adsorptive activity of hydrocarbons, at partial pressure above 10 kPa the sorbent from brown coal has got the most adsorptive activity of hydrocarbons.

Keywords: carbon sorbent, brown coal, hydrolytic lignin, adsorption, aliphatic and aromatic hydrocarbons.

The processes of oil refining, such as catalytic cracking, and catalytic reforming, systems of heating installations of sewage processing, systems of pressure jettisoning, flares, processes of compounding and places of petroleum products storage are the source of volatile hydrocarbons at oil-processing plants [1].

The high-quality active carbons with high cost in particular produced from bituminous coal dust and resin (AG) are applied for adsorption of volatile hydrocarbons at industrial plants [2-4]. Therefore investigations and designs for producing of economical carbon sorbents from cheap and accessible raw materials are of present interest. The application of brown coal and also man-caused wastes in particular hydrolytic lignin as initial materials is promising for producing of carbon sorbents.

Earlier it was noted that sorbents from brown coal and hydrolytic lignin have rather high adsorptive capacity in the processes of phenol's and oil-product's adsorption from aqueous solutions in the wide

varying range of phenol 20-500 mg/l, oil products – 60-380 mg/l [5,6]. And the application of brown coal sorbent was rather effective at adsorption of nitrogen oxides from the gaseous phase [7-9].

The study of brown coal's and hydrolytic lignin's properties at adsorptive processes of volatile hydrocarbons from a gaseous phase is the aim of this study.

Experimental

Carbon sorbent from brown coal (BCS) was produced on semi-industrial installation by one-step process of simultaneous carbonization and activation in fluidized bed reactor [10]. B2 rank of Borodinsky coal was used as a starting raw material. The initial coal has the following characteristics (% wt.): $W^r - 11,2$; $A^d - 6,3$; $C^{daf} - 72,4$; $H^{daf} - 4,8$; $N^{daf} - 0,8$; $S^d - 0,2$. 13-14 kg of coal on a dry coal basis were admitted to the reactor. The temperature was varied in the range 700-750 °C. The concentration of steam in air-steam mixture was 30 % vol., the concentration of oxygen was 4,5-5,0 % vol. The interval residence of coal particles in the reactor was varied in the range 15-45 min.

Carbon sorbent from hydrolytic lignin of Krasnoyarsk biochemical plant (LAC) was produced in fixed bed reactor. Hydrolytic lignin has the following characteristics (% wt.): $W^r - 3,6$; $A^d - 1,6$; $V^{daf} - 63,4$; $C^{daf} - 72,3$; $H^{daf} - 4,1$. Vertical steel reactor with inner diameter 43 mm and height 500 mm was used for producing of carbon sorbent. The sample of hydrolytic lignin was heated up to the temperature 500 °C in the flow of nitrogen. Hydrolytic lignin was pyrolyzed at these conditions during 1 h. After that the temperature was increased up to 800 °C and activating mixture was started to put into the reactor. The activating mixture was consisted from steam and nitrogen. The sample of hydrolytic lignin was activated during 0,5 h at the 0,25 kg/kg steam on a dry hydrolytic lignin basis.

The physical and chemical, adsorptive properties of carbon sorbents have been obtained on described techniques [11, 12]. Micropore volume and BET surface area have been obtained at the sorptomatic ASAP.2400.VI.00. on the basis of adsorption-desorption isotherms of nitrogen. For micropore volume and BET surface area calculation a method of Broekhoff de Boer was applied [13, 14]. An exiccator method at 25 °C was used for the determination of an equilibrium statically ability to benzol [15].

For evaluation of carbon sorbent's adsorptive activity the method of adsorptive isotherm's determination from chromatographic data (elution chromatograms) was applied [16-18]. For determination of adsorptive isotherms the specific conditions were obeyed always. The diffusion processes and kinetic of adsorptive exchange couldn't perturb the profile of chromatographic peak largely. These conditions comply if acute boundaries of chromatographic peak are vertical, but spreading boundaries of chromatographic peak (back boundaries for used hydrocarbons) are the same for different probe's volumes of hydrocarbons. The used technique has the following advantages: simplicity, a high rate of a determination, necessity of small amounts of hydrocarbon. But it has one limitation. The carrying out adsorptive isotherms is possible only for partial pressure which corresponds with the used amount of hydrocarbon.

The adsorptive determinations have been obtained on a gas chromatograph LCM-80 with a hot-wire detector, a steel U-bend column. The chromatographic column with length 10 cm and inner diameter 0,4 cm was used for adsorptive study. The carrier gas is helium; the rate of gas throughput is 40 ml/min.

For the experimental study the grinded in size less 0,5 mm and dried at 105 °C during 3 h carbon sorbent was weighted accurate to 0,1 mg. After that the carbon sorbent was put into the steel chromatographic column. Before testing the carbon sorbent in the column was heated during 20 h in the flow of helium at 200 °C. The liquid samples of hydrocarbons were injected into the chromatographic column by the calibrated micro-syringe. For adsorptive investigations the hydrocarbons of chromatographic specification were used. Pentane, hexane, heptane, octane were selected as aliphatic hydrocarbons and benzol, toluol, *o*-xylo were selected as aromatic hydrocarbons for adsorptive investigations. Before every injection of hydrocarbon the carbon sorbent in the column was heated at 200 °C for a removal of hydrocarbon's traces. The chromatographic determinations were carried out at column's temperature 100 °C. The method of graphical integration was applied for calculation of adsorptive isotherms. The measured value exhibits an error of less 5 % of the indication.

Results and discussion

Some physical and chemical characteristics of produced carbon sorbents are presented in the Table.

The carbon sorbents BCS and LAC have got the closely spaced values of total pore volume (0,53; 0,68 cm³/g) and BET surface area (590; 632 m²/g). But these sorbents are differentiated on the structure of pores. Sorbent LAC has got the micropore volume three times as large as sorbent BCS. And also they have got the substantially equilibrium statically ability to benzol (at 25 °C): 495 and 187 mg/g for BCS and LAC accordingly.

The adsorption isotherms of volatile hydrocarbons by carbon sorbents BCS and LAC are presented on Fig. 1 and 2. The sorbent BCS have a rather high activity at the adsorption of volatile hydrocarbons (Fig.1). At partial pressure 1-2 kPa adsorptive activity of sorbent BCS is 350-550 μmol/g for aliphatic hydrocarbons and 550-800 μmol/g for aromatic hydrocarbons. And when the partial pressure of hydrocarbons was increased up to 15-20 kPa the adsorptive activity of sorbent BCS increases to 800-1200 μmol/g for aliphatic hydrocarbons and to 1150-1500 μmol/g for aromatic hydrocarbons. The value of aliphatic hydrocarbon's adsorption increases at the series pentane → hexane → heptane → octane. At partial pressure below 10 kPa the value of aromatic hydrocarbon's adsorption increases at the series

Physical and chemical properties of carbon sorbents

Indices	Sorbents	
	BCS	LAC
Moisture, % wt.	9,8	0,3
Ash content, % wt.	13,7	3,5
Bulk density, g/dm ³	668	336
Total pore volume (BET), cm ³ /g	0,53	0,68
Micropore volume (BET), cm ³ /g	0,14	0,42
BET surface area, m ² /g	590	632
Ability to iodine sorption, %	51	70,1
Equilibrium statically ability to benzol at 25 °C, μmol/g (mg/g)	6336 (495)	2393 (187)

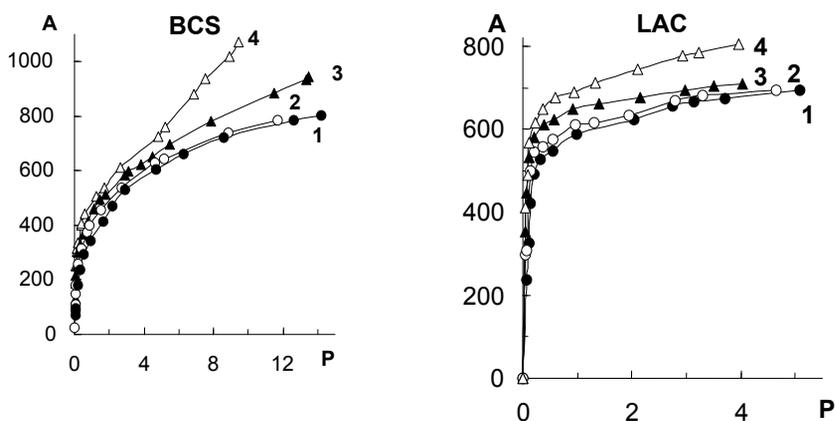


Fig. 1 Isotherms (A, $\mu\text{mol/g}$) of volatile aliphatic hydrocarbons adsorption by carbon sorbents BCS and LAC at temperature $100\text{ }^\circ\text{C}$ (P – partial pressure, kPa): 1 – pentane, 2 – hexane, 3 – heptane, 4 – octane

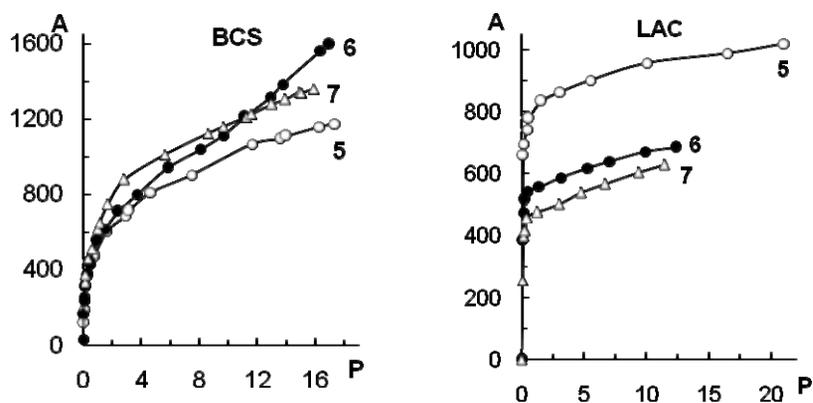


Fig. 2 Isotherms (A, $\mu\text{mol/g}$) of volatile aromatic hydrocarbons adsorption by carbon sorbents BCS and LAC at temperature $100\text{ }^\circ\text{C}$ (P – partial pressure, kPa): 5 – benzol, 6 – toluol, 7 – *o*-xylol

benzol \rightarrow toluol \rightarrow *o*-xylol; but partial pressure above 10 kPa the value of aromatic hydrocarbon's adsorption increases at the series benzol \rightarrow *o*-xylol \rightarrow toluol.

At the adsorption of volatile hydrocarbons by sorbent LAC (Fig.2) the order of aliphatic hydrocarbons in series of adsorption's increasing is the same as at the adsorption of volatile hydrocarbons by sorbent BCS. At the adsorption of volatile aromatic hydrocarbons by sorbent LAC in comparison with the adsorption by sorbent BCS the opposite order was noted. The adsorption of volatile aromatic hydrocarbons by sorbent LAC increases at the series *o*-xylol \rightarrow toluol \rightarrow benzol. Apparently this phenomenon connects with a geometrical structure of pores of produced from hydrolytic lignin sorbent.

At the adsorption of volatile aliphatic hydrocarbons below partial pressure 4-6 kPa sorbent LAC has more high activity to 200-50 $\mu\text{mol/g}$ in comparison with the sorbent BCS. Apparently these data are due to its more developed pore structure (its pore volume is higher at 1,3 times then pore volume of sorbent BCS) and also to interaction of functional groups (owing to hydrogen bonds) on a surface of a

sorbent [19]. At rather closely spaced values of BET surface area (630 m²/g and 590 m²/g for sorbents LAC and BCS accordingly) sorbent LAC has the 2,4 times higher contribution of micropore volume (0,62) then sorbent BCS (0,26).

At partial pressure more 6 kPa the substantial adsorption's increasing of aliphatic hydrocarbons by sorbent BCS is observed. These data point to most quantity of mesopores (transport pores) at sorbent BCS as for many porous materials produced from brown coal in comparison with sorbent LAC [20, 21].

At the adsorption of volatile aromatic hydrocarbons sorbent LAC has higher activity in comparison with sorbent BCS only at the adsorption of volatile benzol during up partial pressure 6kPa. At the adsorption of volatile toluol and *o*-xylol at partial pressure below 0,5-1,0 kPa sorbents BCS and LAC have practically the same activity. However at partial pressure above 1 kPa sorbent BCS exceeds sorbent LAC in adsorptive activity on 50-600μmol/g and 250-700μmol/g for the adsorption of volatile toluol and *o*-xylol accordingly.

The adsorptive isotherms of volatile hydrocarbons by sorbent BCS (Fig. 1, 2) are classified as second type isotherms on BET classification [2]. These data corroborate the existence of large quantity of mesopores and macropores along with micropores. And also these data are evidenced about the exhibition of polymolecular adsorption. The adsorptive isotherms of volatile hydrocarbons by sorbent LAC (Fig. 1, 2) are classified as first type isotherms or classical isotherms of Langmiur's type. They could approximate by the theory of monomolecular adsorption in micropores.

The activities of sorbents BCS and LAC are compared with the activity of commercial active carbon AG-2. As the adsorption of volatile hydrocarbons by powder sorbents BCS and LAC were studied the active carbon AG-2 was grinded to grain size less 0,5 mm. The sorbent BCS has the most statically activity at 2,6 and 1,5 times higher then sorbents LAC and AG-2 accordingly.

The adsorptive isotherms of volatile benzol by carbon sorbents are presented on Fig.3. As for sorbent LAC the adsorptive isotherm of volatile benzol by carbon sorbent AG-2 is the first type isotherm on BET classification [2]. At partial pressure 1-10 kPa the adsorptive ability on the volatile benzol of sorbent AG-2 is higher on 370-20 μmol/g and 70-20 μmol/g then for sorbents BCS and LAC accordingly. At

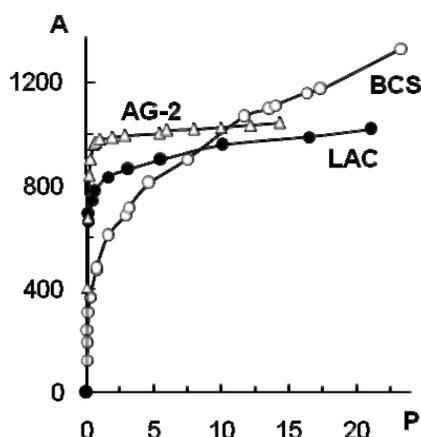


Fig. 3. Isotherms (A, μmol/g) of volatile benzol adsorption by carbon sorbents at temperature 100 °C (P – partial pressure, kPa)

partial pressure 10-15 kPa the difference at the adsorption of volatile benzol by sorbents AG-2 and LAC is remained at the level of 20 $\mu\text{mol/g}$. But this difference increases on sorbent BCS at 70 $\mu\text{mol/g}$ in comparison with sorbent AG-2. At further increasing of partial pressure more 15 kPa sorbent AG-2 is compared unfavorably with sorbent BCS at the quantity of adsorptive ability. At partial pressure 23 kPa the adsorption of volatile benzol by sorbent BCS is 1330 $\mu\text{mol/g}$. The presented data have been obtained on the dynamic conditions. They aren't inconsistent with presented in Table data on statically activity of carbon sorbents.

Conclusions

Sorbents from brown coal and hydrolytic lignin can be used for purification of gaseous emissions at the plants of chemical, oil-processing and coal-processing industry.

At the conditions of relatively high partial pressure (more 10 kPa) of volatile aliphatic and aromatic hydrocarbons for the purification of gaseous emissions brown coal sorbent BCS could can substitute the high-cost commercial sorbent as AG-2. At the conditions of relatively low partial pressure (below 10 kPa) of hydrocarbons sorbent LAC from hydrolytic lignin is recommended to use.

For deficiently high abrasion resistance presented sorbents aren't advisably regenerated. Presented sorbents once will be used. The used sorbents are utilized. Obtained sorbents have a rather low mechanical strength and can not be reused. It is suggested to utilize the spent sorbents by the burning in the energetic installations.

References

1. Protection of the atmosphere from the industrial pollution: Reference book.: In two parts. Part1. Translation from English. /Edited by Kalvert S., Inglund G.M. Moscow: Metallurgy, 1988. 760 p.
2. Kel'cev N.V. Fundamentals of adsorption technology. Moscow: Chemistry, 1984. 592 p.
3. Cleaning of technological gases. /Semenova T.A., Leites I.L., Axelrod Yu.V., Markina M.I., Sergeev S.P., Kharkovskya H.N. 2-nd ed. corrected and supplemented. Moscow: Chemistry, 1977. 488 p.
4. Serpionova H.N. Commercial adsorption of gases and vapors. Moscow.: High School, 1969. 416 p.
5. Eremina A.O., Golovina V.V., Shchipko M.L., Burmakina E.V. Adsorption of phenol from aqueous solutions by carbon sorbents //Journal of Applied Chemistry. 2000. V.73. N2. P. 254-257.
6. Shchipko M.L., Eremina A.O., Golovina V.V. Adsorbents from carbonaceous raw materials of Krasnoyarsk region //Journal of Siberian Federal University. Chemistry. 2008. N1. P.166-180.
7. In-depth processing of brown coals to liquid fuels and carbon materials /B.N.Kuznetsov a.o.; Executive Editor G.I.Gritsko. Novosibirsk: Publishing House SB RAS, 2012. 212 p.
8. Shchipko M.L., Eremina A.O., Golovina V.V., Rudkovsky A.V. Production and study of brown coal adsorbents for gas cleaning from nitrogen oxides //News universities. Chemistry and Chemical Technology. 2009. V.52. N.1. P.56-61.
9. Shchipko M.L., Kuznetsov B.N., Eremina A.O., Golovina V.V. Brown coal adsorbents for flue gas cleaning from nitrogen oxides //Power Engineer. 2009. V.1. P.29-31.
10. Shchipko M.L., Yangolov O.V., Kuznetsov B.N. Activated carbon processing. RU Patent №2051096 // Bulletin of inventions, 1995. №36.

11. Kienle X., Bader Oe. Active carbons and their commercial application. Leningrad: Chemistry, 1984. 216 p.
12. Kolyshkin D.A. Active carbons: Reference Book. Leningrad: Chemistry, 1985. 56 p.
13. Fenelonov V.B. Introduction to physical chemistry for developing of supra-molecular structure of adsorbents and catalysts. Novosibirsk: Publishing House IC SB RAS, 2002. 414 p.
14. Fenelonov V.B. Porous carbon. – Novosibirsk: Publishing House IC SB RAS, 1995. 518 p.
15. Vyakhirev D.A., Shushunova A.F. Manual on gaseous chromatography. 2-nd ed. Moscow: Higher School, 1987. 335 p.
16. Experimental methods on adsorption and molecular chromatography. /Edited by Yu.S.Nikitin, R.S.Petrova. 2-nd ed. corrected and supplemented. Moscow: Publishing House MGU, 1990. 318 p.
17. Selves J.-L., Abraham M.H., Burg P. A new method of the explanation of liquid properties in terms of molecular interactions //Fluid Phase Equilibria. 1998. V.198. P.69-82.
18. Burg P., Abraham M.H., Cagniant D. Methods of determining polar and non-polar carbonaceous adsorbents. The contribution of the linear solvation energy relationship approach //Carbon. 2003. V.41. P.867-879.
19. Lignins (Structure, properties and reactions) /Edited by. K.V.Sarkanen, K.X.Ludwig; Translation from English. Moscow: Forestry industry, 1975. 632 p.
20. Chudakov M.I. Commercial application of lignin. 3-rd ed. corrected and supplemented. Moscow: Forestry industry. 1983. 200 p.
21. Kuznetsov B.N., Shchipko M.L., Kuznetsova S.A., Tarabanko V.E. New approaches to processing of solid organic materials. Krasnoyarsk, 1991. 372 p.
22. Perederiy M.A., Surinova S.I. Fundamental fields on application of adsorbents which are produced from fossil coals // Chemistry of Solid Fuels. 1997. V.3. P.56-61.

Адсорбция паров алифатических и ароматических углеводородов на углеродных сорбентах из бурого угля и гидролизного лигнина

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Изучена адсорбция паров алифатических и ароматических углеводородов на углеродных сорбентах, полученных из бурого угля и гидролизного лигнина. Углеродные сорбенты получены методами пиролиза и парогазовой активации. Для адсорбционных исследований выбраны в качестве алифатических углеводородов: пентан, гексан, гептан, октан, а в качестве ароматических углеводородов: бензол, толуол, о-ксилол. При парциальном давлении углеводородов до 10 кПа более высокую сорбционную способность показал сорбент, полученный из гидролизного лигнина; а при парциальном давлении более 10 кПа – сорбент, полученный из бурого угля.

Ключевые слова: углеродный сорбент, бурый уголь, гидролизный лигнин, сорбция, алифатические и ароматические углеводороды.
