

Properties of Sorbents from Brown Coal

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The surface and sorptional properties of carbonaceous materials prepared from brown coal and their relation to minerals content and coal bulk density as technologically important parameters of starting coal were described.

From brown coal of North Bohemian Brown Coal District the chars were prepared and activated with CO₂ in a large-scale laboratory unit. Their surface and sorptional properties were investigated. It was found that mineral matters/ash content favourably affects the mesoporosity development in chars/activated chars as the sorption capacity increased with increasing ash content in chars. No influence of ash content on the macroporosity was observed. With the activated chars, both the inner surface and sorption capacity showed the maximum in the burn-off range of 41–64 %. In this connection, optimization of the process is discussed. The mass balance of carbonization and size analysis of chars and activated chars were carried out and the influence of ash content and coal bulk density was discussed.

Beside hard coals and anthracites, brown coals represent a suitable raw material for the production of sorbents as their chars and activated chars have a developed porous system. Moreover, big pores facilitating the access of adsorbed substances to the inner surface are formed [1].

The sorption and physical properties of the sorbents produced from brown coals are affected by a number of factors: the starting coal parameters, the preparation of coal, its preoxidation, and processing conditions: grain size, heating rate, final temperature of carbonization, temperature and time of activation, and medium [2]. Therefore, it is useful to investigate relations between technologically important parameters of brown coal and of the process on one hand and the complex of surface, sorptional and physical properties of materials prepared on the other.

In our case, the surface properties of sorbents from brown coal and their relation to mineral matters content and coal bulk density as technologically important parameters of starting coal and of the process were investigated.

EXPERIMENTAL

After preliminary research [3], brown coal from the open-cast coal mine CSA of North Bohemian Brown Coal District was used. The proximate analysis of coal samples including the ultimate analysis of coal CSA is presented in Table 1. From the CSA coal, ten chars were prepared by the low-temperature carbonization in a large-scale laboratory unit. For the carbonization,

Table 1. Proximate Analysis and Bulk Density of Coal Samples Used

Sample	$w_i/\%$				d g dm ⁻³
	Moisture	A ^d	VM	S _t ^d	
1	8.1	3.2	55.1	1.2	522
2	9.9	4.5	54.4	1.6	506
3	13.3	4.7	53.3	1.2	487
4	17.6	3.3	53.9	0.7	466
5	25.1	3.6	55.1	1.0	421
6	6.6	6.5	56.0	1.3	524
7	7.1	7.5	50.4	1.2	519
8	6.0	7.5	48.7	1.7	525
9	5.9	8.1	50.7	1.5	527
10	7.4	8.2	49.6	1.2	518

A^d – ash (dry sample), VM – volatile matter (dry ash-free sample), S_t^d – total sulfur (dry sample), d – bulk density. Ultimate analysis of coal CSA, $w_i/\%$ (i): 76.38 (C), 6.30 (H), 0.92 (N), 0.83 (S), 15.57 (O_{diff}) (dry ash-free sample).

a 7 kg-test oven with cooling system and a gas holder including a GC analyzer were used. The sample (6–7 kg) with the grain size of 4–10 mm was thermally treated at the heating rate of 5 °C min⁻¹. The coal bulk density varied in the range of 421–527 g dm⁻³ (Table 1). The final treatment temperature was 640–650 °C, the soaking time at the final temperature was 60 min. The proximate analysis of the chars obtained is presented in Table 2.

Table 2. Proximate Analysis of Chars Obtained

Char	$w_i/\%$			
	Moisture	A ^d	VM	S _t ^d
1	1.8	6.6	3.9	0.7
2	2.7	9.1	3.7	0.9
3	1.6	9.1	4.7	1.0
4	2.7	6.2	3.8	0.7
5	2.6	6.8	3.9	0.8
6	0.9	13.0	5.3	1.4
7	2.8	13.6	2.2	1.5
8	2.0	14.1	2.8	1.3
9	0.9	14.4	2.1	1.4
10	0.7	14.8	1.9	1.5

For symbols see Table 1.

Two chars obtained were further activated with carbon dioxide. For the activation, the char 4 with a lower-ash content (ash = 6.2 %, dry sample, Table 2) and the char 9 with a higher-ash content (14.4 %, dry sample, Table 2) were taken. The char sample (0.3 kg) with grain size of 4–10 mm was activated at 900 °C in a quartz reactor by carbon dioxide at the flow rate of 3.8 dm³ min⁻¹. Twelve samples of activated chars were prepared at various times of the partial gasification (15–320 min). From the char 4, the activated chars 1–5 were prepared, further, from the char 9 the activated chars 6–12 were prepared. Proximate analysis of the activated chars obtained is presented in Table 3.

For the surface characterization, the BET surface (S_{BET}) of the chars and activated chars was measured (nitrogen isotherm at 74 K, Sorptomatic 1800, Erba). The micropores surface (S_{micro}) and the micropores volume (V_{micro}) were determined with the same device from the carbon dioxide isotherm at 298 K. The mesopores volume (V_{meso}), the macropores volume

(V_{macro}), the sum of the meso- and macropores surface ($S_{\text{m+m}}$), and the (apparent) mercury density (ρ_{Hg}) were determined by high-pressure mercury porosimetry (Porosimeter 2000, Erba). The real density (ρ_r) was determined pycnometrically with methanol [4], the helium density (ρ_{He}) was measured by the helium pycnometry (Autopycnometer 1320, Micrometrics). Further, the iodine adsorption number (I) according to the standard method [5] was evaluated.

Image analysis of the big macropores (width over 4 μm) of chars and activated chars was also carried out. A width, the formfactor, and the mean density of abundance of pores (abundance) were measured on 30 mm polished sections by means of Textur Analyse System Leitz. The abundance was expressed as a number of pores in mm² of the area of polished section. The porosity of big pores was expressed as a total area of cuts of pores (%). The rest (100 - porosity) was considered as the wallicity. The mean thickness of the walls was determined microscopically according to [6, 7].

RESULTS AND DISCUSSION

Table 1 shows that lower-ash (1–5) and higher-ash coal samples were chosen for experiments. Therefore, the chars with lower-ash content (1–5, Table 2) and the chars with higher-ash content (6–10, Table 2) were obtained.

From Table 3 it is obvious that with increasing value of the burn-off the total sulfur and also the organic sulfur increased in the samples of both series. From comparison of total and organic sulfur content it follows that the organic sulfur is the prevailing form in activated chars.

Surface properties of chars are presented in Table 4. For individual quantities, results obtained are not very different except the values of V_{meso} and $S_{\text{m+m}}$. The methanol, helium, and mercury density

Table 3. Proximate Analysis of Activated Chars

Activated char	$w_i/\%$					
	Burn-off	Moisture	A ^d	VM	S _t ^d	S _o ^{daf}
1	9.4	0.6	7.0	1.2	0.7	0.7
2	15.7	1.0	7.5	2.0	0.9	0.7
3	19.8	0.8	8.2	1.0	0.9	0.8
4	32.1	1.0	9.0	1.4	1.1	1.0
5	42.0	0.7	11.9	1.7	1.1	1.0
6	12.6	0.7	14.3	1.4	0.9	0.8
7	32.0	1.2	17.2	1.5	1.4	1.2
8	34.8	0.8	21.1	1.5	1.8	1.2
9	36.2	0.8	20.1	1.6	1.7	1.2
10	41.4	0.9	23.0	1.8	1.8	1.2
11	64.4	0.8	27.2	1.9	1.9	1.3
12	68.0	0.8	28.5	1.9	2.4	1.6

S_o^{daf} – organic sulfur. For other symbols see Table 1.

Table 4. Surface Properties of Chars Obtained

Char	$\rho_i / (\text{g cm}^{-3})$			$V_i / (\text{cm}^3 \text{g}^{-1})$			$S_i / (\text{m}^2 \text{g}^{-1})$		
	real	He	Hg	micro	meso	macro	micro	m + m	BET
1	1.78	1.62	1.15	0.159	0.011	0.127	589	1.85	129
2	1.82	1.66	1.23	0.147	0.015	0.113	546	2.66	183
3	1.85	1.68	1.26	0.144	0.011	0.119	539	1.74	159
4	1.77	1.69	1.63	0.153	0.010	0.138	567	1.63	135
5	1.82	1.65	1.50	0.151	0.009	0.106	560	1.50	168
6	1.79	1.63	1.12	0.144	0.027	0.157	534	4.13	214
7	1.88	1.71	1.27	0.146	0.020	0.108	546	2.71	204
8	1.83	1.76	1.22	0.141	0.038	0.145	523	4.61	214
9	1.84	1.67	1.25	0.150	0.021	0.101	577	2.73	227
10	1.87	1.71	1.20	0.151	0.033	0.145	559	6.81	228

ρ_i – real, helium, and mercury density, V_i – micro-, meso- and macropores volume, S_i – surface of micropores, sum of meso- and macropores surfaces, and BET surface.

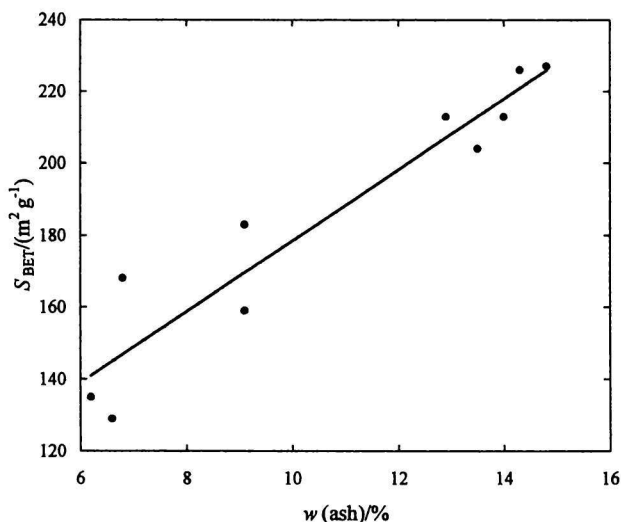


Fig. 1. The dependence of the BET surface on the ash content in chars.

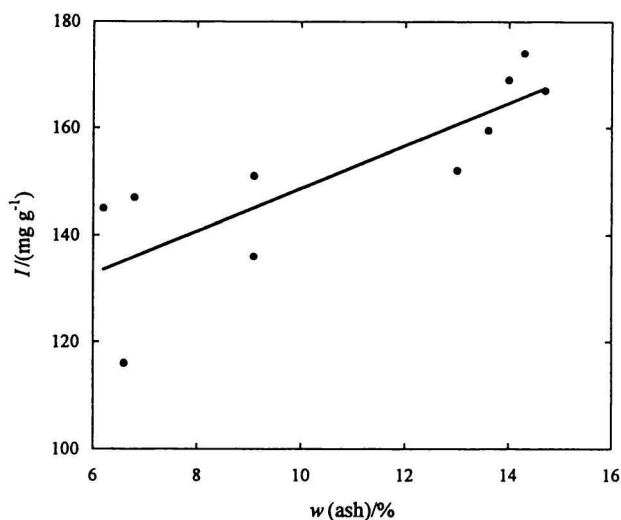


Fig. 2. The dependence of the iodine adsorption number (I) on the ash content in chars.

did not reflect changes of the bulk density of starting coal (Table 1, samples 1–5) or the ash content. Therefore, an influence of these parameters is more subtle. It was found that the S_{BET} increases with increasing ash content in chars (Fig. 1).

Also iodine adsorption number increased with ash content (Fig. 2). An increase of the sorption capacity with increasing ash content in chars from Kansk-Achinsk lignites was also recognized by the authors of Ref. [8]. From Table 4 it is evident that the mesopores volume and the surface $S_{\text{m+m}}$ of the chars with lower-ash content (1–5, Table 2) were markedly lower than those of the chars with higher-ash content (6–10, Table 2). Therefore, the development of mesoporosity was more extensive for chars with higher-ash content. Because S_{micro} was practically independent of the ash content as it follows from Tables 4 and 2, we can conclude that mineral matters affect favourably the mesoporosity development.

From a comparison of the micro-, meso-, and

macropore data (Table 4) it follows that the chars are largely microporous. A part of the microporosity is utilized during adsorption from solutions. The evaluation of an iodine sorption proved that the I value of chars (116–174 mg g^{-1}) depends linearly on S_{BET} in the range of 129–228 $\text{m}^2 \text{g}^{-1}$ (correlation coefficient 0.896). For activated chars (see later), S_{BET} correlated closely with the I value (121–473 mg g^{-1}) in the range of 70–427 $\text{m}^2 \text{g}^{-1}$ (correlation coefficient 0.977). From these data it follows that the I values obtained were satisfactory. Low values of the V_{meso} and the sum of the meso- and macropore surface ($S_{\text{m+m}}$) indicate that mesoporosity is relatively small. However, its contribution to sorption ability is significant as mentioned data prove.

From Tables 2 and 4 it follows that the macropores volume did not depend on the ash content in chars. In this connection, big macropores with width higher than 4 μm were investigated by the image analysis and their parameters and distribution were determined.

Table 5. Image Analysis of Big Macropores of Chars

Char	Mean width	FF
	μm	
1	67.98	1.37
2	64.86	1.34
3	82.82	1.24
4	61.83	1.37
5	43.40	1.36
6	76.96	1.25
7	42.82	1.27
8	75.57	1.34
9	92.36	1.27
10	105.49	1.09

FF – the formfactor.

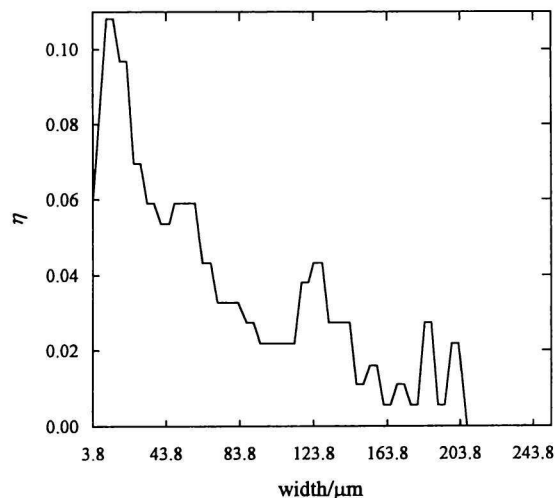
For individual chars, the porosity ranged between 21–42 %, the wallicity between 58–79 %. The abundance of macropores in question varied in the wide range of 47–242 mm^{-1} . The variability of porosity/wallicity, and variability of the abundance is accounted to the heterogeneity of the big macropores. Results of the other image measurements are presented in Table 5. Because the formfactor of cuts of the pores was 1.24–1.37, it is evident that big macropores were elliptical with the form nearing the circle. Therefore, it was possible to correctly quantify the width of the pores by one parameter. From the data in Table 5 it follows that the mean width of big macropores of lower-ash chars (1–5) was comparable with that of higher-ash chars (6–10). According to independent microscopic measurements [7] the mean width for a lower-ash char was 88 μm and 93 μm for a higher-ash char. These values are in an agreement with our measurements presented in Table 5.

The typical distribution of macropores over 4 μm is illustrated in Fig. 3. No substantial difference between distributions of the big macropores of lower-ash chars and higher-ash chars was observed. No influence of coal bulk density was found in this connection.

The mean thickness of walls of big pores was also evaluated. Two chars, 4, ash content 6.2 % and 9, ash content 14.4 % (Table 2), were tested. For char 4 the mean thickness was 129 μm , for char 9 it was 126 μm . These data are in a good agreement with the work [7]. The values obtained served for comparison with the wall thickness of activated chars (see later).

The mass balance of the carbonization was carried out. If we consider dry coal as 100 mass %, then 53–58 mass % of char, approximately 9–11.5 mass % of tar, 5–5.5 mass % of water, and 26–32 mass % of gas including losses were obtained. A slightly increasing yield of char with increasing bulk density of the carbonized coal was observed.

A size analysis of chars was also carried out. As a lump material, the fractions over 4 mm were considered. Results showed that a maximum yield 69–82 %

**Fig. 3.** Distribution of big macropores with the width over 4 μm for char 1.**Table 6.** Size Analysis of Chars Obtained from Coal Samples

Char	$w_i/\%$		
	0–4 mm	4–8 mm	8–10 mm
1	26.2	69.0	4.8
2	24.9	70.0	5.1
3	26.0	65.1	8.9
4	25.1	69.7	5.2
5	21.2	72.1	6.4
6	16.2	79.0	4.8
7	12.3	81.1	6.6
8	11.8	82.4	5.8
9	18.6	74.7	6.7
10	13.2	81.0	5.8

was obtained from the fraction 4–8 mm (Table 6). We find the yield of lump fractions as a sufficient one. From Table 6 it is obvious that higher yields of the lump material were obtained in the case of higher-ash chars (6–10).

On the whole, the development of pore structure was extensive enough during low-temperature carbonization. Both the mass balance of carbonization and the yield of the main fraction 4–8 mm seem to be favourable. Therefore, the chars represent a suitable, inexpensive and accessible material for sorptional purposes, moreover, they can be alternatively used as smokeless fuel. The broader utilization requires an activation.

Surface properties of the chars were improved by partial gasification with CO_2 . Surface characteristics of activated chars are presented in Table 7. The improvement of surface properties in comparison with initial chars (Table 4, 4 and 9) is demonstrated on

Table 7. Surface Properties of Activated Chars

Activated char	$\rho_i/(g\text{ cm}^{-3})$		$V_i/(cm^3\text{ g}^{-1})$			$S_i/(m^2\text{ g}^{-1})$		
	He	Hg	micro	meso	macro	micro	m + m	BET
1	1.70	1.36	0.166	0.011	0.105	613	0.306	—
2	1.74	1.35	0.167	0.021	0.094	614	1.385	138
3	1.74	1.29	0.159	0.013	0.122	559	1.851	139
4	1.73	1.15	0.165	0.004	0.186	600	0.616	276
5	1.74	1.29	0.184	0.004	0.121	680	0.667	318
6	1.70	1.19	0.169	0.050	0.145	618	5.762	130
7	1.97	1.38	0.156	0.061	0.168	568	6.292	202
8	1.75	1.16	0.164	0.035	0.200	595	5.420	303
9	1.74	1.00	0.163	0.062	0.194	596	7.689	338
10	1.75	1.04	0.198	0.035	0.195	717	4.366	394
11	1.74	0.87	0.178	0.048	0.320	653	4.932	427
12	1.74	1.02	0.151	0.039	0.199	551	4.721	302

For symbols see Table 4.

S_{BET} and S_{micro} . The development of porous system is shown also by volume quantities V_{micro} , V_{meso} , and V_{macro} . However, no development of mesoporosity in the case of activated chars from initial lower-ash char (activated chars 1–5, Table 7, in comparison with initial char 4, Table 4) was observed. On the contrary, the considerable development of mesoporosity in activated chars from higher-ash char (activated chars 6–12, Table 7 in comparison with initial char 9, Table 4) was found. Again, it follows that higher-ash content affects favourably the mesoporosity development. Owing to this effect, the $S_{\text{m+m}}$ of activated chars from higher-ash char increased 2–3 times in comparison with the starting char, but practically no changes of $S_{\text{m+m}}$ of activated chars from lower-ash char were observed. The sorption capacity improvement is clear from comparison of the I values of chars and activated chars (see above).

The dependences of the surface parameters on the burn-off pass through a maximum in the region of roughly 41–64 % burn-off (Tables 3 and 7, Fig. 4). (Also the dependence of the I value on the burn-off passed through a maximum in this region.) Therefore, the conditions of the sorbents preparation must be optimized. It requires above all an improvement of the surface parameters of the initial char by the optimization of the process parameters of the carbonization. While higher carbonization temperature leads to development of microporosity, the high heating rate of carbonization ($\Phi \cdot 10^2\text{ }^\circ\text{C min}^{-1}$) supports the development of mesoporosity during following activation [9]. The higher carbonization temperature (700–750 °C) seems to be the solution, because the use of high heating rates is problematic from the practical point of view. Moreover, the development of mesoporosity is supported by mineral matter, as was proved above for the chars prepared at low heating rate ($5\text{ }^\circ\text{C min}^{-1}$) and as the dependence of S_{BET} on the ash content shows (Fig. 5). Another way is a chemical pretreat-

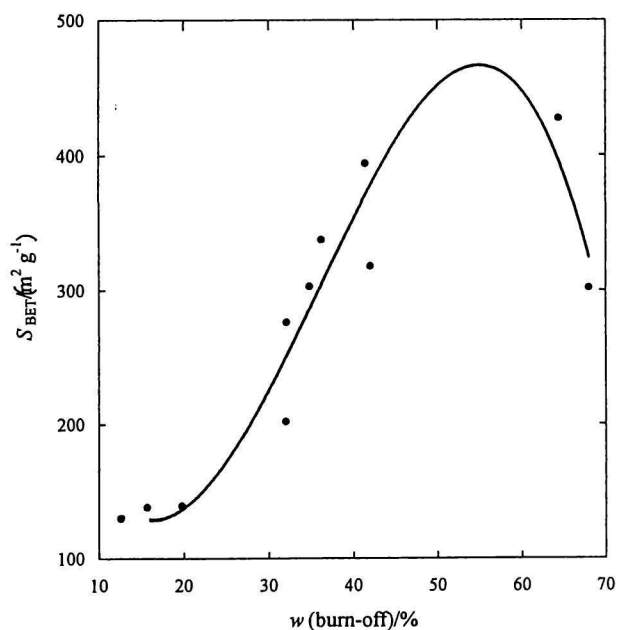


Fig. 4. The dependence of the BET surface on the burn-off for the activated chars prepared.

ment of coal by NaOH or mineral acids [10–13].

As Fig. 4 proves, under optimal conditions of activation a peak S_{BET} is obtained. Analogical dependence was observed in [14] during steam activation of low-rank coals. As the rise of S_{BET} before the maximum is a consequence of the inner surface development, the drop of S_{BET} after the maximum is connected with a reduction of the wall thickness and collapse of the walls [14]. In our case the changes in the distribution of the wall thickness of big macropores (Fig. 6) and a reduction of mean wall thickness (see later) of activated chars were observed. While walicity of char 4 was 62 %, that of activated char obtained (4) was only 53 %. Similarly the walicity of char 9 was 65

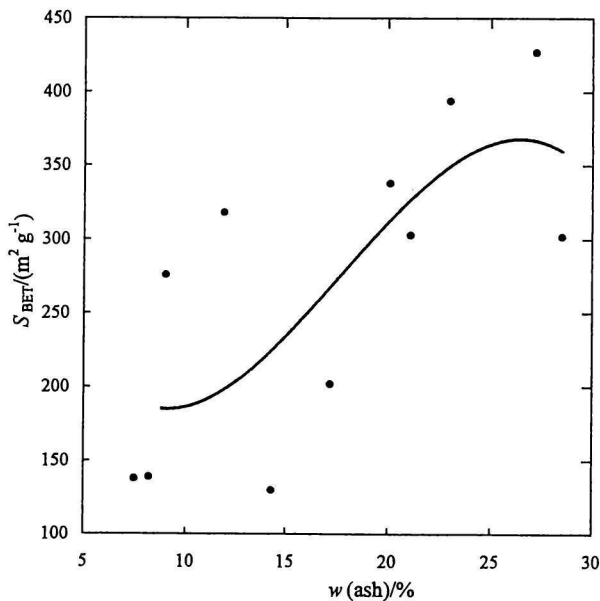


Fig. 5. The dependence of the BET surface on the ash content of the activated chars prepared.

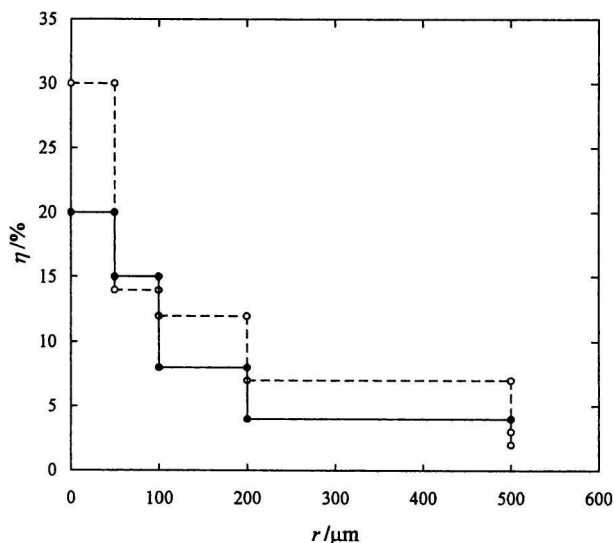


Fig. 6. Distribution of the wall thickness (r) of big macropores in char 9 (dashed line) and in activated char 9 (solid line).

%, while resulting activated char 9 showed the value of 50 %.

Microscopic measurements proved that the thickness of walls of big pores of studied materials varied in the wide range of 70–162 μm . According to microscopic measurements [7] the mean value of the wall thickness was 127 μm for a low-ash char (4) and 125 μm for a high-ash char (9). These data are in a good agreement with our measurements (125 μm for char 4 and 123 μm for char 9). According to our measurements activated chars showed reduction of mean wall

thickness to 97 μm (4) and 95 μm (9). Variability of the wall thickness means that the big pores were heterogeneously developed in chars and activated chars. The values of the wall thickness are important for the strength of studied materials. Correlative mechanical properties of chars and activated chars, above all the problem of abrasion will be discussed in another work.

For application, a suitable size of activated particles is necessary. Therefore, the size analysis of the activated chars obtained was performed. From initial 4–10 mm chars the activated chars of the size under 8 mm were obtained. The yield of the main 4–8 mm fraction was 62–88 %, the yield of the 1–4 mm fraction was 11–28 % and for the 0–1 mm fraction the 1–10 % yield was found. These results are favourable, because the yield of the lump material (over 4 mm) was sufficient.

Surface properties, sorption capacity, and grain size of the chars and activated chars prepared show that these materials are sufficient as industrial sorbents for the treatment of waste water and air.

CONCLUSION

From the CSA brown coal of North Bohemian Brown Coal District the chars in the large-scale laboratory unit were prepared and activated with CO_2 . Their surface and sorption properties were investigated, also in relations to ash content and coal bulk density. It was found that mineral matters/ash content affect favourably the mesoporosity development in chars/activated chars, and the sorption capacity. No influence of the ash content and bulk density on the macroporosity was observed. With the activated chars, both the inner surface and sorption capacity showed the maximum in the range of 41–64 % burn-off. Therefore, for sorbent production the optimization of the process conditions, above all a higher final carbonization temperature or a chemical pretreatment is necessary. The wall thickness was found as good or acceptable with the chars/activated chars. The favourable mass balance and the yields of lump fractions make possible the preparation of inexpensive materials in question. The chars and activated chars from brown coal will be tested as cheap single sorbents for treatment of waste water, air, and gases.

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