INFLUENCE OF THE SUPERCRITICAL TOLUENE EXTRACTION OF BROWN COALS ON THE DEVELOPMENT OF POROSITY DURING CARBONIZATION AND STEAM GASIFICATION

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INTRODUCTION

The supercritical gas extraction belongs to relatively new technologies of coal processing (1-7). In most cases the research was directed towards the yield of obtained extracts and their physico-chemical nature. Less attention was given to studies of the properties of the extract residues, which in this process are obtained in significant amounts and are usually utilized for combustion or gasification.

The work presented in this paper is focused on the extract residue, with the aim to obtain some information as to what extent the supercritical gas extraction of brown coals might modify their ability to develop a given capillary structure in the processes of carbonization and steam gasification.

EXPERIMENTAL

From Polish brown coal mines, five coals were chosen to represent samples with different content of humodetrinite. The petrographic and chemical analyses of these coals are presented in Table 1.

In a separate research project (8), supercritical gas extraction of these coals was carried out (toluene at 410°C and 13 MP_a; extract yields are given in Table 1), and the extracted residues were delivered to the authors of the present work for further investigations. Extracted residues from coals L, B, R, S, and T were designed as EL410, EB410, ER410, ES410 and ET410 respectively.

In order to obtain, from the initial brown coals (BC), such samples which would, as to their heat treatment temperature (HTT), correspond to the extract residues (EBC410), the BC samples were carbonized in an aluminum retort (5°C/min, atmosphere of pyrolytic gases) to HTT=410°C. After maintaining this temperature for 30 minutes, the obtained BC410 chars were cooled to room temperature in a stream of argon. The chars BC410 and EBC410 were further carbonized to HTT=900°C in a rotary furnace (5°C/min, Ar), maintaining this temperature also for 30 minutes and cooling the chars BC900 and EBC900 in argon. Results of proximate and ultimate analyses of the chars shows Table 2.

Gasification of the BC900 and EBC900 chars with water vapor was performed at 800°C in a thermogravimetric apparatus, to 50% burn-off of the organic substance of the chars; water vapor was generated in an electrically heated flask at constant water level, to ensure a flow rate of 30 $dm^3 h^{-1}$ the diameter of the reactor tube being 40 mm.

On all the investigated carbonacous samples, sorption measurements of benzene, carbon dioxide and water vapor at 25°C were carried out, using a gravimetric vacuum apparatus (McBain quartz springs).

RESULTS AND DISCUSSION

The influence of supercritical toluene extraction of brown coals on the course of their carbonization and gasification with water vapor (determined in a thermogravimetric apparatus) is shown in Figures 1 and 2 respectively.

As was to be expected, the yields of chars from extract residues are significantly greater than those obtained for the non-extracted coals (Figure 1). The plots in Figure 2 indicate that no definite influence of supercritical extraction of brown coals on the reactivity of their chars towards water vapor was found. This seems to be in accord with the results of Yuh and Wolf (4), concerning the catalytic effect of K_2CO_3 in the steam gasification of chars from a low rank coal and its supercritical toluene extract residues.

Figure 3 shows and example of sorption isotherms of benzene, carbon dioxide and water vapor (on chars from initial and extracted brown coal L); for respective chars from brown coals B, R, S and T, similar shapes of corresponding isotherms were found. In all cases the same characteristic trends could be noticed. Benzene sorption isotherms are characterized by a pronounced differentiation of shapes and amounts absorbed, depending on the HTT of the chars, their gasification and, in case of HTT=410°C, on extraction. For the initial coals and the non-gasified chars, isotherms of type I are obtained, with low amounts adsorbed (although benzene adsorption on the EBC410 samples distinctly exceeds the adsorption on the chars BC410); a low-pressure hysteresis occurs in all cases. After partial gasification (activation) with water vapor, the phenomenon of low-pressure changes into type II, and the amounts adsorbed strongly increase. Contrary to what was observed with benzene isotherms, the adsorption of carbon dioxide is much less influenced by the kind of considered char. Water vapor isotherms, when passing from initial coals to chars with increasing HTT and further to activated chars, show - in the low-pressure region - a systematic decrease of amounts adsorbed; here no influence of extraction was noted.

Basing on benzene sorption data, the pore size distribution of mesopores was calculated (9,10), assuming a cylindrical shape of the pores (Figure 4). The resulting micropore volumes (in case of isotherms showing low-pressure hysteresis the adsorption brance of the hysteresis loop was considered) were in good agreement with the values of Wo, calculated by means of the Dubinin-Radushkevich (DR) equation (11) - Table 3. In the benzene micropore volumes, super and ultramicropores were distinguished (12), estimating from the course of the isotherms, the regions of relative pressures corresponding to the primary and secondary process of adsorption: the amounts adsorbed at relative pressure of 0.01 were attributed to primary adsorption. The volumes of still narrower ultramicropores, indicated in the histograms shown in Figure 4, were estimated basing both on benzene and carbon dioxide adsorption isotherms, evaluated according to the DR equation. The volumes of ultramicropores accessible only for the CO_2 molecules, were calculated as the difference between the Wo values from carbon dioxide and benzene adsorption.

In these calculations the density of the adsorbed carbon dioxide at 25°C was taken as 1.038 $g.cm^{-3}$ (11,13). Before the calculation of the Wo values from the benzene and carbon dioxide adsorption isotherms the experimental isotherms (Figure 3) were corrected for adsorption in the mesopores, basing

on respective standard isotherms on non-porous carbonaceous materials (Spheron 6 and Vulcan 3).

Table 4 shows surface area values corresponding to benzene, carbon dioxide and water vapor adsorption. The cross-sectional areas of the molecules of these adsorbates were taken as 0.4375nm^2, 0.185 nm^2 and 0.106 nm^2 correspondingly. The values of S_{BET,C_6H_6} were calculated from the benzene adsorption isotherms were calculated from the benzene adsorption isotherms according to the BET equation. The obtained surface areas were compared with the values of S_{B,C_6H_6}, resulting from the amounts of benzene adsorbed at point B of the isotherms, and were found to be usually a little lower: the slope of the linear regression plot presented in Figure 5 is 0.89 (r=0.996).

Contrary to this, a very good accord is observed between the values of the surface areas S_{B,C_6H_6} and those calculated as folows: the values of micropore volumes $W0_{DR,C_6H_6}$, calculated from corrected (for mesoporosity) benzene isotherms, were expressed in surface area units, and to the obtained results: S_{wo,DR,C_6H_6}, the values of the surface areas of mesopores (S_{mes}) were added. The slope of the corresponding regression plot was now very close to unity (1.04), with r also equal 0.996. It seems possible that in case of benzene adsorption, the point a_m, resulting from application of the BET equation, corresponds mainly to the volume filling of micropores (strongly enhanced heat of adsorption), and is not identical with the point B of the isotherm, where the amounts adsorbed might correspond not only to the volumetrically filled micropores, but also to the formation of a monolayer in the mesopores (this sum would correspond to a less enhanced heat of adsorption).

The surface areas S_{CO2} were calculated as $S_{Wo,DR,CO2} + S_{mes}$. For initial brown coals these surface areas exceed significantly the respective values obtained on the basis of benzene adsorption, pointing to an important molecular sieve effect in these samples (this can also be seen from Table 3). This effect also strongly pronounced in the non-activated chars, seems to be to some extent still present even after their gasification to 50% burn-off.

The values of surface areas corresponding to adsorption of water vapor, were obtained, expressing in terms of surface areas the amounts of water adsorbed at p/po = 0.6 (14). To gain some indication concerning the polarity of the surface of the investigated samples, the ratio S_{H2O}/S_{CO2} was calculated; here S_{CO2} and adsorption data were taken (as a parameter apt to described the total surface area accessible for the H_2O molecules), because of the mentioned molecular sieve effect for the benzene molecules.

For a clearer demonstration of the influence of supercritical extraction of brown coals on the parameters of their capillary structure formed during carbonization and steam activation, in Figures 6 and 7 the ratios of values of chosen parameters for chars from the extracted and non-extracted coals are presented.

CONCLUSIONS

The results obtained during this research, seem to furnish some indications concerning the kind of modifications, caused by supercritical toluene extraction of brown coals, in the course of development of their porosity

during carbonization and steam gasification.

The porous system of initial brown coals is composed mainly of very fine, benzene inaccessible, ultramicropores ($V_{ult,CO2}$) - Figure 4a. The high oxygen content in these coals (Table 1) indicates a significant concentration of oxygen functional groups and explains a high ratio of S_{H2O}/S_{CO2} (Table 4).

In case of chars corresponding to HTT=900°C, as well as in these chars after their steam gasification (to burn-off of 50%), the influence of coal extraction is very small: the ratios of all the considered parameters (Figures 6 b, c and 7 b, c) are very close to unity. This would mean that at HTT=900°C a very similar kind of porosity is being formed as the result of removal of the more volatile parts of the organic substance of coals, no matter if this was caused solely by the process of pyrolysis, or also by supercritical gas extraction (Figure 4 c, d).

However at a lower HTT (410°C) as can be noted, that the supercritical gas extraction of the coals causes a distinctly greater development of the porosity than that which takes place on carbonization only (Figure 4 b). The extraction favorizes all the considered kinds of benzene accessible porosity, and this trend is the more pronounced, the narrower the pores. The highes ratios of pore volumes in the HTT 410°C chars from extracted and non-extracted coals were obtained for the benzene accessible ultramicropores ($V_{ult,CO2}$)BC are below unity. These extremely small ultramicropores, which develop strongly on heating of the non-extracted coals to 410°C, partly disappear (compared with respective initial coals), when the process of supercritical toluene extraction is carried out. It is possible that these ultramicropores, present in the initial coals, might play the role of centres, facilitating the extraction process, in which benzene accessible ultra- and supermicropores are formed, at the expense of the pre-existing, only CO_2 accessible, ultramicropores.

This would perhaps also point to a special significance of the CO_2 surface area: a parameter able to detect in a carbonaceous material the presence of a very fine porous system (inaccessible for other adsorbates), the existence of which seems to facilitate the development of further porosity in thermochemical processes.

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Table 1. The Characteristics of Polish brown coals

Symbol of brown coal:	L	B	R	S	T
Groups of macerals (vol. %, mineral matter free):					
- humotelinite	3.0	12.6	12.7	20.6	30.4
- humodetrinite	88.4	74.5	71.8	60.2	47.4
- humocollinite	1.5	1.4	6.5	16.9	10.5
- liptinite	5.7	10.6	5.8	1.0	10.9
- inertinite	1.4	0.9	3.2	1.3	0.8
Group components of the organic substance (%, daf):					
- bitumens	2.5	3.4	5.9	2.3	3.4
- humic acids (free)	55.9	22.3	65.1	18.8	14.7
- humic acids (total)	66.5	33.4	81.1	25.4	16.9
- residue	31.0	63.2	13.0	72.3	79.7
Yield of toluene extract (%, daf):	23.9	27.3	42.9	34.4	36.4
Proximate analysis:					
- total moisture (%, raf)	60.3	59.3	55.0	53.5	52.0
- ash (%, dry)	6.6	5.9	12.4	7.3	7.0
- volatile matter (%,daf)	55.0	56.1	62.1	55.2	58.1
Ultimate analysis (%, daf):					
- carbon	65.8	65.7	66.9	67.5	69.5
- hydrogen	5.7	6.1	5.9	5.2	5.8
- nitrogen	0.7	0.8	0.5	0.7	0.8
- (O + S) by diff.	27.8	27.4	26.7	26.6	23.9
Total sulfur (%, dry):	0.7	0.6	7.2	2.0	2.1

Table 2. Proximate and ultimate analyses of chars from inital and toluene extracted brown coals (%)

Symbol of initial brown coal	Chars from: brown coals					Chars from: extract residues				
	W^a	A^d	VM^{daf}	C^{daf}	H^{daf}	W^a	A^d	VM^{daf}	C^{daf}	H^{daf}
HTT=410°C										
L	1.5	7.5	37.1	70.5	4.5	3.2	9.0	30.3	76.7	4.0
B	2.6	7.0	37.2	71.5	4.6	1.5	8.4	28.4	75.7	4.3
R	1.8	16.7	31.9	79.0	4.5	2.3	19.8	33.8	79.3	4.3
S	1.7	8.6	32.1	75.1	4.3	2.0	9.7	30.5	77.4	4.1
T	2.6	8.1	34.5	74.2	4.7	1.7	10.4	24.5	78.9	4.1
HTT=900°C										
L	1.6	10.5	5.7	89.7	1.2	1.8	12.7	6.2	90.0	1.4
B	1.8	10.0	5.7	92.5	1.1	1.3	11.2	6.1	93.8	0.9
R	3.0	20.6	4.2	97.5	1.0	2.8	25.0	5.5	98.8	1.1
S	1.9	12.6	4.7	92.6	1.3	1.4	13.9	4.1	94.1	1.2
T	2.4	11.7	4.9	93.4	0.9	1.9	13.6	5.1	93.2	1.1

Table 3. Parameters Wo ($cm^3.g^{-1}$) and B of the DR equation for benzene and carbon dioxide adsorption at 25°C

Symbol of initial brown coal	Adsorbate							
	C_6H_6		CO_2		C_6H_6		CO_2	
	Wo	$Bx10^6$	Wo	$\beta Bx10^6$	Wo	$Bx10^6$	Wo	$\beta Bx10^6$
	Brown coals				Extract residues			
L	0.006	4.05	0.086	3.59				
B	0.004	4.22	0.068	3.66				
R	0.006	6.50	0.066	3.01				
S	0.002	4.14	0.077	3.46				
T	0.003	5.57	0.061	3.46				
	HTT=410°C							
L	0.021	4.39	0.128	3.97	0.081	1.35	0.144	3.38
B	0.017	3.12	0.115	3.63	0.089	2.53	0.176	3.70
R	0.017	3.49	0.111	3.80	0.076	1.60	0.149	3.59
S	0.016	4.22	0.122	3.54	0.100	2.11	0.152	3.50
T	0.017	2.95	0.093	3.54	0.104	2.49	0.140	3.59
	HTT=900°C							
L	0.085	0.93	0.163	2.15	0.072	1.18	0.156	2.33
B	0.081	1.10	0.177	2.53	0.076	1.35	0.167	2.58
R	0.035	2.20	0.212	2.70	0.053	2.11	0.192	2.66
S	0.042	2.91	0.200	2.62	0.044	2.45	0.187	2.66
T	0.040	3.29	0.194	2.49	0.058	2.95	0.194	2.58
	Chars HTT=900°C steam activated at 800°C (BO=50%)							
L	0.096	1.31	0.102	2.70	0.085	1.31	0.095	2.87
B	0.064	1.27	0.095	2.79	0.070	1.10	0.095	2.70
R	0.145	0.50	0.173	3.14	0.143	0.56	0.169	3.19
S	0.104	1.98	0.166	3.06	0.097	2.29	0.128	2.95
T	0.174	2.07	0.207	3.26	0.166	2.01	0.189	3.17

Table 4 Surface areas ($m^2.g^{-1}$) based on benzene, carbon dioxide and water vapor adsorption at 25°C

Symbol of initial brown coal	S_{BET}	S_{CO2}	$0.6\ S_{H2O}$	$0.6\ S_{H2O}/S_{CO2}$	S_{BET}	S_{CO2}	$0.6\ S_{H2O}$	$0.6\ S_{H2O}/S_{CO2}$
	Brown coals				Extract residues			
L	24	226	482	2.13				
B	21	179	458	2.56				
R	26	174	422	2.43				
S	21	202	436	2.15				
T	29	160	333	2.08				
				HTT=410°C				
L	63	336	371	1.10	292	378	445	1.17
B	55	302	362	1.20	274	462	416	0.90
R	74	292	316	1.08	224	392	430	1.10
S	47	321	348	1.08	256	400	421	1.05
T	55	244	273	1.12	266	368	505	1.37
				HTT=900°C				
L	216	428	385	0.90	211	410	357	0.87
B	211	465	389	0.84	192	439	338	0.77
R	108	557	479	0.86	161	505	466	0.92
S	108	526	396	0.75	132	492	380	0.77
T	84	510	419	0.82	148	510	413	0.81
	Chars HTT=900°C steam activated at 800°C(BO=50%)							
L	458	500	158	0.32	424	452	139	0.31
B	390	455	135	0.30	387	453	131	0.29
R	482	577	405	0.70	501	584	311	0.53
S	477	669	237	0.35	432	554	198	0.36
T	516	661	351	0.53	469	613	334	0.54

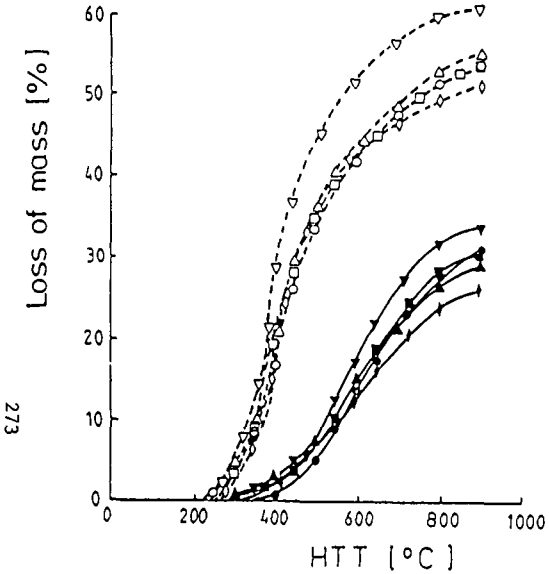

Figure 1 Influence of toluene extraction of brown coals on the course of carbonization ○L, △B, ▽R, □S, ◊T; ●EL, ▲EB, ▼ER, ■ES, ♦ET.

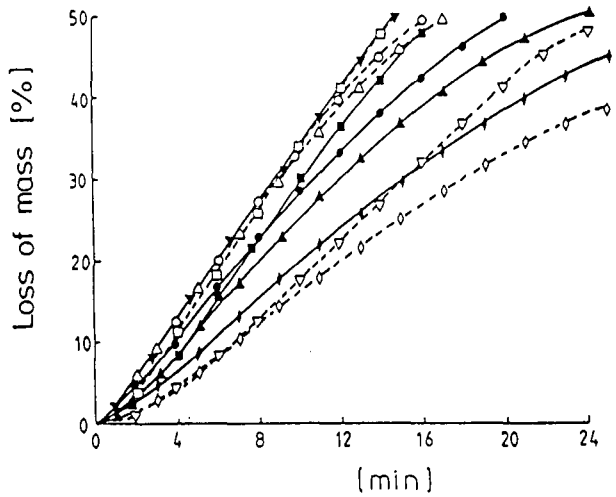

Figure 2 Steam gasification at 800°C of chars (HTT= 900°C) from initial (○L, △B, ▽R, □S, ◊T) and toluene extracted (●EL, ▲EB, ▼ER, ■ES, ♦ET) brown coals.

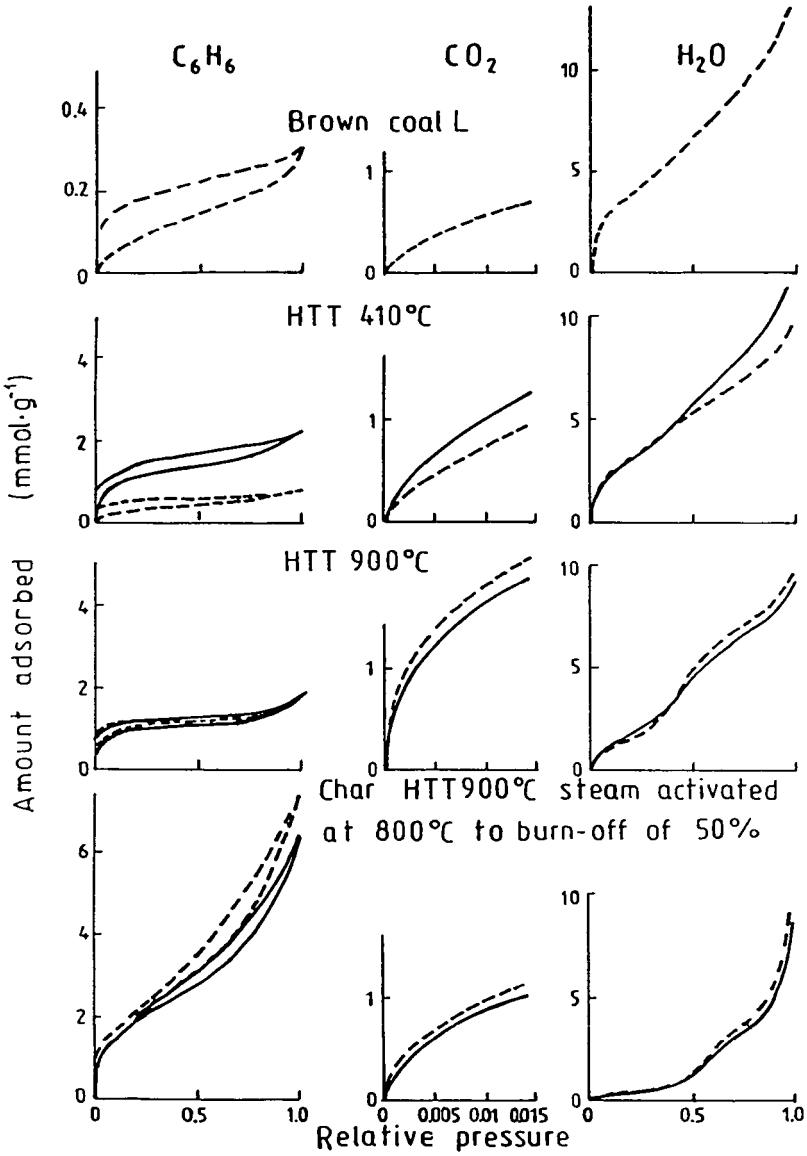

Figure 3 Isotherms (25°C) of C_6H_6 ad- and desorption, CO_2 adsorption and H_2O adsorption. – – – sample from brown coal L; ——— sample from extract residue.

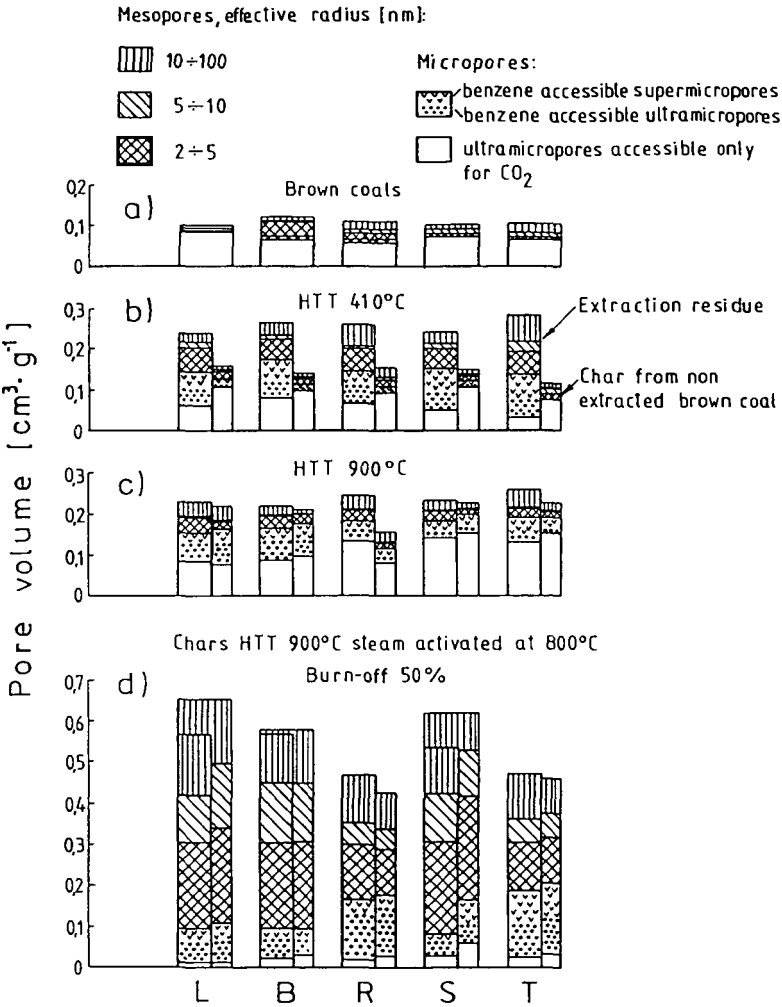

Figure 4 Influence of toluene extraction of brown coals on the pore size distribution in chars obtained on carbonization and steam activation.

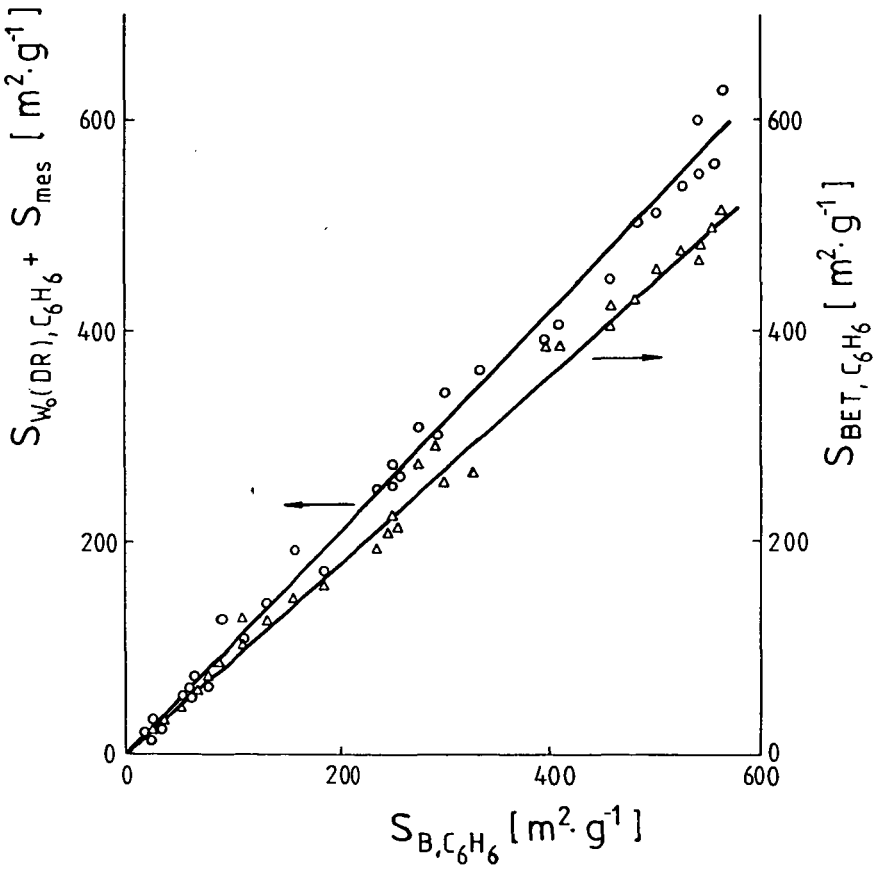

Figure 5 Relations between benzene surface areas of investigated carbonaceous samples estimated in different ways.

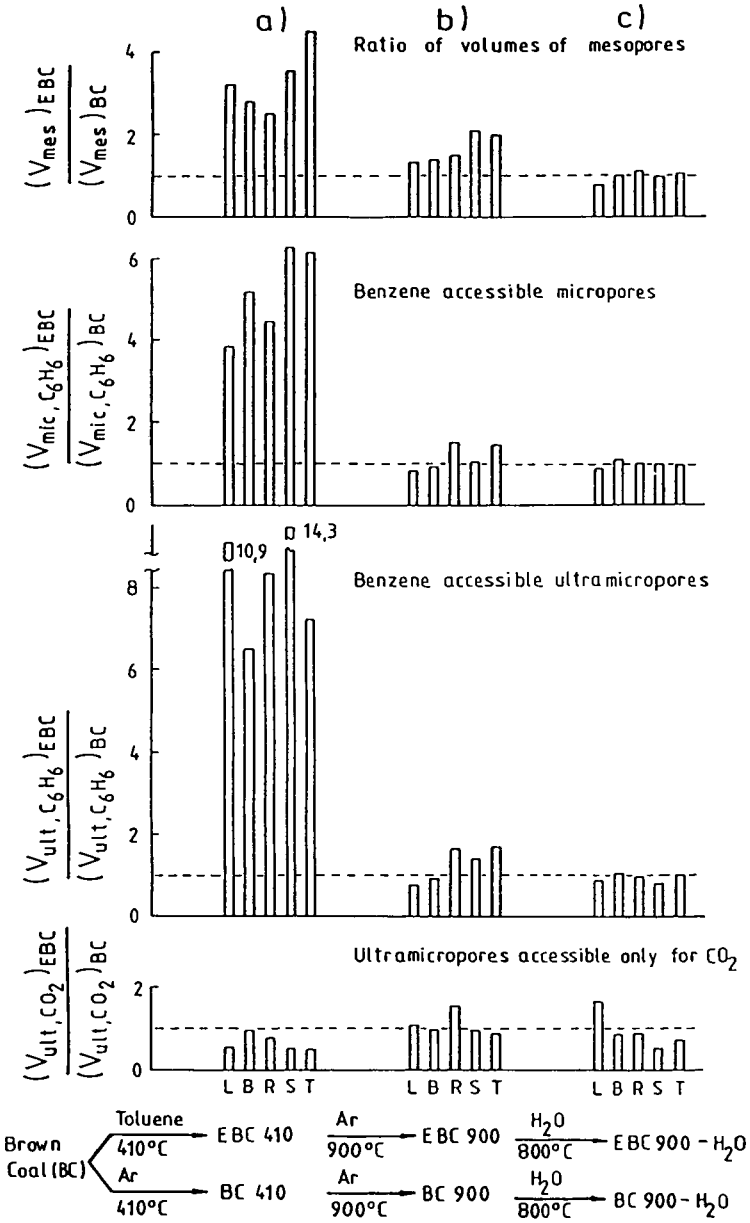

Figure 6 Infuence of toluene extraction of brown coals on the development of pore volume during carbonization and steam activation.

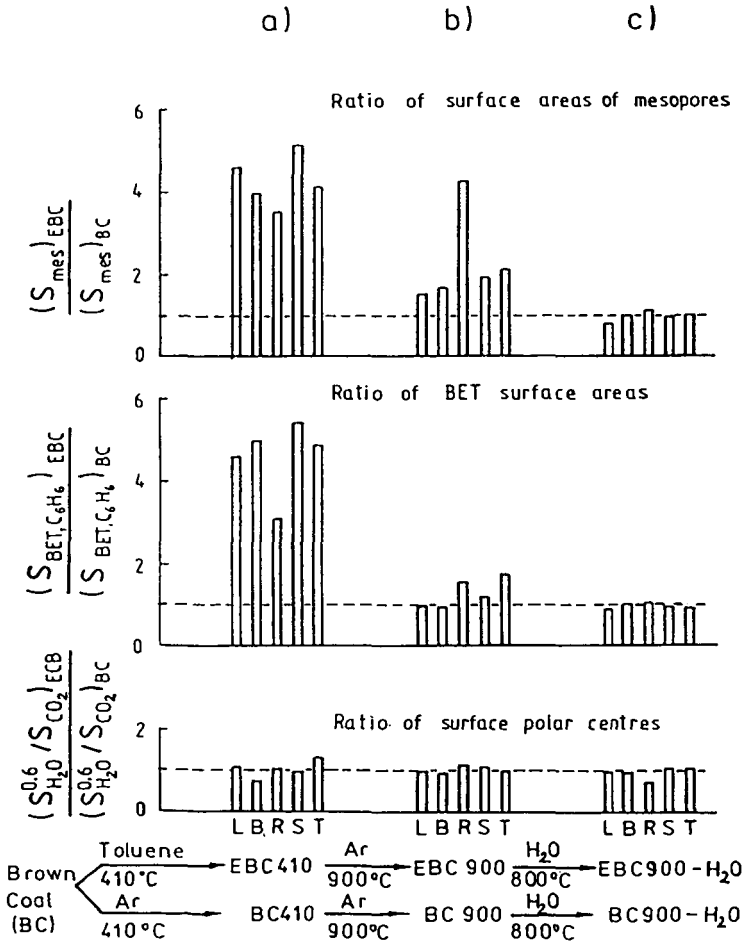

Figure 7 Influence of toluene extraction of brown coals on the development of surface area and surface polarity during carbonization and steam activation.