Slovak brown coals as a feedstock for the active coke production

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Slovenské hnedé uhlie ako surovina pre výrobu aktívneho koksu

V článku sa venuje pozornosť možnostiam výroby aktívneho koksu zo slovenského hnedého uhlia Bane Cígeľ. Príprava aktívneho koksu bola uskutočnená v laboratórnych podmienkach a v poloprevádzke. Surové uhlie sa podrobilo vysokoteplotnej pyrolýze v retorte s pevným roštom, v klasickej rotačnej peci, ako aj vo fluidnom reaktore. Následne boli určované adsorpčné charakteristiky získaného aktívneho koksu, ktoré sa porovnávali s charakteristikami komerčne vyrábaného koksu. V príspevku sa taktiež diskutujú možnosti aplikácie pripraveného aktívneho koksu v technológiách ochrany životného prostredia.

Kľúčové slová: hnedé uhlie, pyrolýza, aktívny koks, adsorpcia.

Introduction

A widespread application of adsorptive processes in the environmental protection technologies depends first of all on prices of adsorbents put on the market. The problem is especially important in poor countries of the Central Europe with highly degraded environment. The question how to produce cheap adsorbents and from which materials has been studied by the group of experts in the framework of the international research project EUREKA EU 1436 ”Cheap adsorbents”. These adsorbents are products of thermal processing of carbonaceous raw materials and their specific surface is usually in the range 200-500 $m^2.g^{-1}$. An active coke is a typical representative of this group. The active cokes from brown coal have been produced for many years in Europe (Ewers et al., 1993) and their production exceeded the total production of activated carbons of all types. Thus, the active cokes with weak adsorptive properties thanks to their low price and a high supply are commonly applied as the adsorber packing material in adsorptive installations for waste gases final cleaning (power plants, incinerating plants). A continuous operation under a very high flow of gaseous phase and low concentrations of pollutants is a characteristics of such installations.

Raw material

The cost of the adsorbent production is the difference between the price of carbonaceous raw material and the thermal processing of that raw material. The experience indicates that the proper selection of the suitable carbonaceous raw material is mostly the condition which decides on the successful production of the active coke. It is commonly known fact that almost all substances containing elemental carbon can be in practice more or less activated (Heschel et al., 1995) but not all carbonaceous materials can be considered as the attractive raw materials for the adsorbents production.

The following factors decide on their usefulness for the active cokes production:

- ability to form a well developed porous structure during the thermal processing,
- possibility to obtain the product of required parameters including a grain size distribution and high mechanical strength,
- attractive relation between the raw material price and the yield of the final product.

These all three elements have to be verified step by step from the laboratory analyses of raw material, through next technological tests and finally to the economic analysis of the production. In the practice, the starting point of this procedure is to select the relatively cheap coal of a low ash content and a high mechanical strength. For such an initially selected raw material the bench-scale pyrolysis tests must be carried out whose theirs favourable results can only be the starting point for further pilot-

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scale tests. These tests should next indicate the process solutions and technological conditions for the commercial production of the active coke.

A detailed analysis of Slovak brown coals produced in Upper Nitra Mines has shown (Sobolewski et al., 1994) that the coal of "Cigel" Mine is the best raw material for the production of active coke. This raw material after mechanical cleaning is characterised (table 1) by the lowest ash content among all tested raw materials from 3 coal mines in the basin as well as a high mechanical crushing strength determined by the tumbler test. Moreover, the relatively low content of moisture in this coal shows a possibility to obtain the final product of about 30 % yield in relation to the initial raw material. Above mentioned facts allowed to consider the "Cigel" Mine´s brown coal as a potential feedstock for the production of active cokes.

Tab.1. Basic characteristic of Upper Nitra brown coals.

Coal mine :		"Cigel" Mine	"Handlova" Mine	"Novaky" Mine
total moisture	W^r_t	27.0 %	24.3 %	33.9 %
moisture content	W^a	22.5 %	7.3 %	14.0 %
ash content	A^a	10.2 %	33.9 %	27.0%
volatiles	V^a	36.3 %	30.6 %	34.0%
mechanical strength		98.0 %	98.0 %	94.5 %

Technological research

The second important problem which conditions the preparation of the market-attractive active cokes is the proper choice of the technology for their production. To be guided by the rule of minimised production costs at the beginning all concepts of raw materials pre-treatment (oxidation or briquetting) must be excluded. For the same reason, the conventional method of two-stage adsorbent production has to be also rejected. So, only the single-stage process can be seriously considered. This process (usually called pyrolysis) is in practice the combination of raw material drying and its pyrolysis, inner combustion and gasification. All these processes (in the case of industrial production) are realised simultaneously. Considering the complexity of problem the full theoretical model of these processes including the heat, mass transfer and chemical reactions course has not yet been elaborated. Thus, research workers are obliged to do experiments and to explain their results.

Figure 1 presents the yield of the solid product in the different thermal processing for "Cigel" coal against a background of TGA curve supplemented by the drying tests of raw material. Denotations in the Figure 1 indicate the treatment in DFxB (directly heated fixed bed), IFxB (indirectly heated fixed bed), CFB (circulating fluidized bed), BFB (bubble fluidized bed), RK (rotary kiln). The coal drying tests have been carried out in a standard laboratory chamber drier whereas a gravimetric test in the Leco TGA 501 apparatus.

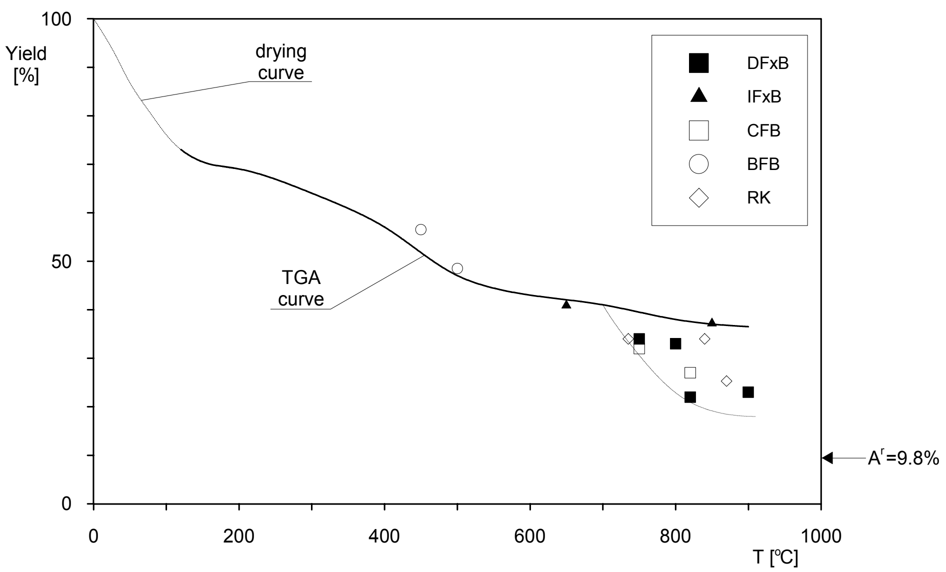


Fig.1. Comparison of the coke yield for different methods of the "Cigel" coal processing with the TGA curve.

For each process and temperature the active coke yield cannot be higher than the value from the TGA curve. At the same time the full gasification and/or burning of the coal substance leads to the yield of about 10 % that corresponds with the ash content in raw material. At temperatures above 700°C, where inner combustion processes of the coal substance, self-oxidation and gasification by process gas as well as some secondary reactions of gaseous products from high-temperature pyrolysis of raw material with carbon intensively take place, we can observe a decrease of the yield for all tested treatment processes, excluding the indirect pyrolysis in fixed bed (IFxB). This observation is agree with our expectations because the IFxB process indeed images the TGA test on a larger scale. We can here sum up that from the defined raw material in a single-stage process the solid product can be obtained of the yield not higher than the value expected from the TGA curve and not lower than the ash content in the initial feedstock. In the case of ”Cigel” coal this range is 10-40 %. At the same time, received products are characterised by different porous structure which depends not only on the final processing temperature but also on the method of the process realisation. The analysis of the Figure 1 indicates that the single-stage processing of ”Cigel” coal in temperatures 700-900°C allows in practice to obtain the solid product of 23-34 % yield. A shift of the lower limit from 10 % to about 20 % results from the fact that the full burning and gasification of the coal substance in raw material is unavailing because is the way to obtain only an ash. A limiting ratio for the product $C^{fix}/A \geq 1$ we accepted as a technological assumption. This means that process can be conducted to 50 % of the limiting ash content in the solid product. In the case of ”Cigel” raw material the yield is about 20 %. The question is whether, such a product will be market-attractive?

Tab.2. Characteristics of active cokes from the ”Cigel” brown coal in comparison with the ”Rheinbraun” product.

Process :		I-stage pyrolysis (DFxB)	II-stage activation (BFB)	I-stage Pyrolysis (”Rheinbraun”)
V^a	[%]	7.7	3.5	2.0
A^a	[%]	42.3	34.9	8.5
water porosity	[cm^3/g]	0.66	1.20	0.54
iodine number	[mg/g]	440	590	500
methylene blue number	[cm^3]	5	10	8
mechanical strength	[%]	91.6	84.0	94.0
product yield	[%]	23	22	-

However, to define the limiting value of the activation level for the ”Cigel” coal, technological tests were carried out. Theirs results are presented in Table 2. So, the single-stage direct pyrolysis in fixed bed (a simulation of rotary kiln conditions) and the typical two-stage processing (carbonisation and activation) in the fluidized bed have been compared. The process was conducted in the both cases to the yield slightly higher than 20 %. The properties of the received activation products have been compared with the properties of commercial active coke produced from brown coal in the single-stage process by the Rheinbraun Brennstoff GmbH (Germany). A comparison of results indicates a possibility to obtain from ”Cigel” coal activates of commercial quality. The received activation products are characterised by a well developed porous structure and a satisfactory mechanical strength. The serious weak point is unfortunately the high ash content but according to the adsorption studies (Finqueneisel et al., 1997) such a product should not be discredited. The best activation level for the product, according to the expectations, was found in products of two-stage process but results of single-stage direct pyrolysis do not differ significantly from the properties of the German active coke. The data presented in Table 2 indicate that the ”Cigel” brown coal can be considered as a potential raw material for the active cokes production.

The next step of tests was to define the thermal conditions and the method of process realisation. These investigations were carried out in a bench scale (3 kg of raw material/test) in the Institute for Chemical Processing of Coal. Table 3 presents the results of these tests for the temperature of about 850°C. They indicate much better properties of the activation product received in the direct heating process which means a direct contact of hot gaseous mixture flowing through a less cold layer of the raw coal material. In this case the special construction of retort allows to simulate the heat and mass transfer conditions in the rotary kiln (Stelmach et al., 1997). In the both direct processes we have obtained active cokes of better sorptive parameters under the same temperature and lower processing time. The third experiment (described as the gasification process) was carried out by adding water steam into the activation gases mixture. An increase of water steam in the activation gases mixture from 19 % v/v to 45 % v/v resulted in the almost 50 % rise of the total pores volume and about 20 % rise of the methylene and iodine numbers. A partial gasification of the coal substance must simultaneously impair a grain physical structure of the product (Komatsubara et al.,

1985) which affects negatively the mechanical strength of the active coke (reduction from 96.1 % to 92.8 %) but the obtained result is still satisfactory. Bench-scale tests have shown in the single-stage allothermal pyrolysis under the temperature 800-850°C and processing time 1.5 h that it is possible to obtain active coke of the 25-30 % yield of product regarding the initial raw material.

Tab.3. Characteristics of the active cokes the from bench-scale (3kg) single-step processing of the "Cigel" brown coal.

Process : heating		Pyrolysis indirect (IFxB)	pyrolysis direct (DFxB)	Gasification Direct (DFxB)
temperature	[°C]	850	800-850	820-850
time	[h]	3.5	1.5	1.5
water porosity	[cm^3/g]	0.28	0.46	0.68
iodine number	[mg/g]	220	370	440
methylene blue number	[cm^3]	1	4	5
mechanical strength	[%]	89.2	96.1	92.8

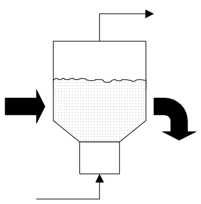
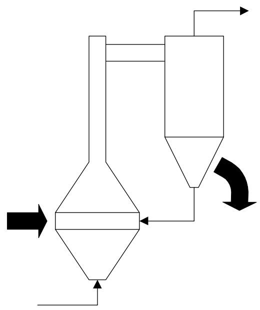
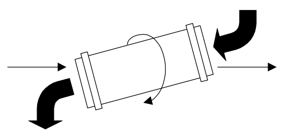
Semi-commercial tests

Semi-commercial tests have to be carried out in order to finally confirm possibilities of obtaining products of commercial properties from the selected raw materials. In our case of "Cigel" brown coal we tested several process and apparatus solutions of the single-stage thermal processing of the raw material received directly from the mine. The following tests were carried out:

- low-temperature pyrolysis in bubble fluidized bed reactor BFB, capacity: 30-50 kg of raw material/h, place: Institute for Chemical Processing of Coal (Zabrze, Poland),
- high-temperature pyrolysis in circulating fluidized bed reactor CFB, capacity: 150-250 kg of raw material/h, place: Institute for Chemical Processing of Coal (Zabrze, Poland),
- high-temperature counter-current pyrolysis in the rotary kiln RK, capacity: 200-400 kg of raw material/h, place: Centre de Pyrolyse de Marienau (Forbach, France).

Tests conditions as well as obtained results are presented in Table 4. The BFB test is cited only for a comparison because, basing on the bench-scale tests, the process temperature has been fixed above 800°C. Two tested methods - CFB and RK - present extremely different heat and mass transfer conditions in the reactor. CFB reactors are characterised by an especially high heat and mass transfer coefficients in the system because of turbulent gas flow in the apparatus. This fact causes an immediate heating of the raw material, a high thermal gradient within a single grain which further reduces the processing time to several minutes, on the one hand and have a negative impact on a grain break-up and impair their mechanical strength on the other hand. An application of the rotary kiln allows then to carry out pyrolysis tests in conservative conditions i.e. under a relatively slow heating of single coal particle and a possibility to separate drying and pyrolysis zones of the rotary kiln length. A

Tab.4. Characteristic of active cokes from single-stage semi-commercial scale processing of "Cigel" brown coal.

Apparatus:	BFB Bubbles Fluidized Bed	CFB Circulating Fluidized Bed	RK Counter-current Rotary Kiln
			
scale:	30 kg/h	150 kg/h	200 kg/h
temperature product yield	450 –500°C 52%	750 - 820°C 30%	730 - 830°C 34%
volatiles V^a porosity specific surface area	32% 0,60 cm^3/g 140 m^2/g	8,0% 0,47 cm^3/g 240 m^2/g	4,3% 1,10 cm^3/g 275 m^2/g

residence time of particles in the reactor in this case is about 30-60 min. Considering the possibilities to reduce costs of the future production of active cokes (Vogt et al., 1997) the tests of destination were carried out in the autothermal process where a heat necessary to support the process was generated by burning the volatile matter involved within the reactor as well as by inner burning of the coal substance and self-oxidation. Both processes proceed only above 600^{o}C and therefore require to be initiated (reactor warm-up) by using an external fuel - natural gas. The yield of the solid product during tests was 30-35 %, according to the expectations.

Evaluation of the products

In order to generate a well developed porous structure in thecoal raw material it is necessary to maintain the activation factors (process temperature and selected composition of the activation gaseous mixture) during a defined time. An analysis of the process conditions in the both apparatuses - CFB and RK - markedly favours the rotary kiln as documented by the properties of the received active cokes (Table 4). At a similar temperature the porosity of the product was more than 2 times higher in the case of the rotary kiln. However the specific surface area as determined by the benzene method was only by 15 % higher for the activation product from RK. These two facts indicate a very extensively developed macroporous structure of the active coke from the rotary kiln. In order to determine the pore diameter distribution in the received active cokes the tests were done by using of the Carlo Eba 2000 Series mercuric porosimeter. The results are presented in Figure 2 and compared with the porosimetric parameters of the initial ”Cigel” coal and the ”Reinbraun” active coke. The bar chart (Figure 2) presents the full range of pore diameters determined by the apparatus as the height of succeeding bars and pore volumes as black part of the bars in the 500-5000 Å range.

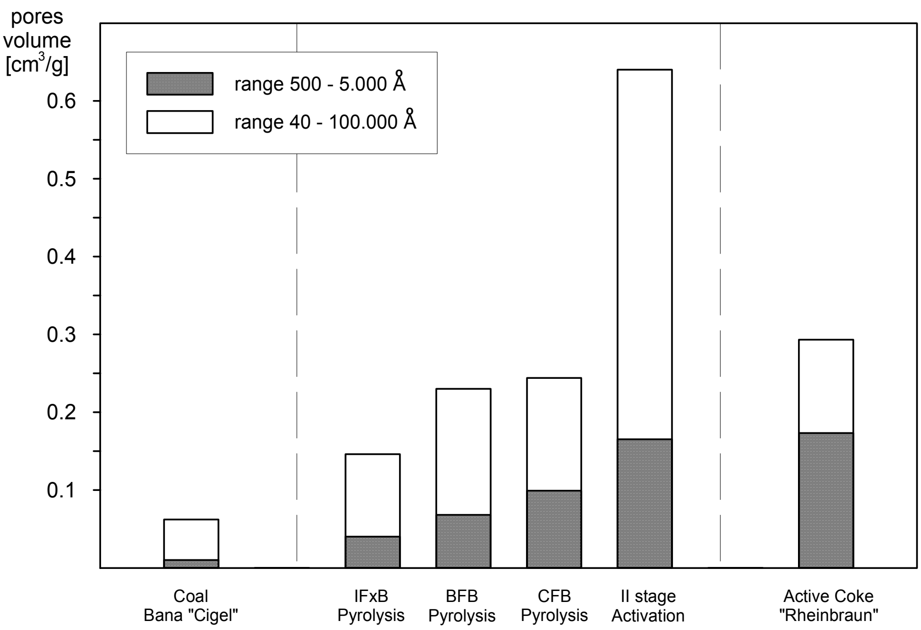


Fig.2. Porosimetric characteristics of the active cokes from the ”Cigel” brown coal.

A commercial active coke should be characterised by a relatively narrow spread of pore diameters. Each carbonaceous raw material is capable to form a characteristic porous structure. However technological processes allow to correct its structure slightly. So, the proper selection of the raw material is a very important parameter. In the case of ”Reinbraun” active coke almost 60 % of the total pore volume was in the 500-5000 Å range and a maximum of its pore distribution function was at about 3000 Å. The ”Cigel” Mine coal was characterised by a lower selectivity of pore diameter distribution and in the case of the CFB processing it allowed to obtain the product for which 40 % of the total pore volume was in the 500-5000 Å range. The test results indicate moreover the relatively broadened maximum of the distribution at 20000 Å for all samples of the activation products received from the tested raw materials, irrespective of the total pore volume. Nevertheless it should be emphasised that the single-stage processing allowed to increase 4 times the total pore volume and about 10 times their volume in the interesting diameter interval. For comparison, Figure 2 presents the porosimetric characteristic of the active coke received from the ”Cigel” coal by the conventional two-stage method. In this case more than the 250% rise of the pore volume was observed in relation to the CFB activation product but only the 60 % rise of pores in the 500-5000 Å range. At the same time the two-stage process caused the higher spread of pore diameters and only 25 % of their total volume was in the interesting interval. Comparing the received activation products with the ”Reinbraun” active coke we can state that the total pore volume of the CFB activation product was slightly lower (by about 15 %) and the pore diameter distribution was wider. An analysis of the results presented in Table 4 allows us to state that the process carried out in RK should result in the product with the porous structure to be near to the German coke but the maximum of the pore diameter distribution for the active coke from Slovak coal will be probably about 20000 Å.

Application of active cokes

The main field of application for active cokes is their using as a packing material for adsorbing of pollutants from the gaseous phase. At first they can be used in a final cleaning process of waste gases from municipal and industrial incinerating plants as well as for an adsorptive desulphurization of combustion gases in power plants. Modern technologies, considering the very large flux of the purified gas, favour solutions with continuous processes and so adsorbers with a gravitational moving of the active coke bed (Kuhn et al., 1990). Typical and widely applied in many of EC countries solutions are made by German companies (leaders in this field, much experienced), e.g. adsorber with a cross phase flow of the Steinmüller Co. (Kubisa et al., 1996) or adsorber with a counter-current flow of the WKV Co. (Witaliński, 1998). The preliminary evaluation of German experts concerning the usefulness of the active coke received from the ”Cigel” brown coal for their adsorbers is positive but the final opinion can be formulated exclusively after several-months pilot-scale tests. The porous structure and mechanical strength of the active coke has been highly appreciated but the high ash content is unfortunately problematic. In respect of adsorption from the gaseous phase the potentially attractive market for the active cokes can be in Japan and South Korea where the new environmental regulations more restrictive to the dioxins and furans emission, have been established from 1998.

The second potentially attractive application of the active cokes is a final cleaning of toxic industrial wastewater (Feldener et al., 1995) from organic substances e.g. PAH and heavy metals. The investigations carried out in the Institute for Chemical Processing of Coal and University of Metz have shown that the active coke from the ”Cigel” coal allows to reduce organic pollutants by more than 50%, determined as TOC reduction, from the biologically purified coke wastewater and by more than 75 % of TOC in the petrochemical wastewater and allows the more than 90 % reduction of some heavy metals in model aqueous solutions (Finqueneisel et al., 1996). The weak point of adsorption from the liquid phase is the relatively high consumption of the adsorbent in the final cleaning process which amounts about 20 kg of the active coke/m^3 of the treated wastewater. For this reason the solution is not preferred especially in the countries of low environmental fees and penalties.

The another problem connected with the implementation of the adsorption processes in the environmental protection technologies is the spent adsorbent utilisation. The problem is especially important in the case of expendable adsorbents as the active cokes are. The standard solution of the problem is to burn coke in the incinerating plants equipped with the developed waste gases purification systems (Schafer et al., 1993). The application of spent active coke as a component for coking blend can be another solution. Thermal conditions in the coking chamber where a blast-furnace coke is produced guarantee a full thermal decomposition of the adsorbed organic substances (Karcz et al., 1997).

Summary

From the result of the bench-scale and semi-commercial tests we can consider the possibility to produce active cokes from Slovak brown coal (”Cigel” Mine). The active coke produced in the autothermal single-stage processing of this raw material in the rotary kiln is characterised by the well developed porous structure and high mechanical strength. These parameters allow us to apply this active coke in the adsorption processes from the gaseous phase as a packing material for adsorbers with the gravitational moving bed.

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