
**CHARACTERISATION OF CARBONIZATE PRODUCED FROM VELENJE
LIGNITE IN LAB-SCALE REACTOR**

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Abstract

In year 2002 laboratory carbonization of lignite samples was done in a rotary kiln reactor at five different temperatures (550, 600, 650, 700, 750°C), four different retention times (15, 30, 60 and 120 min) and three different particle size categories (4-10, 10-20 and 20-40 mm). Later on specific surface determination of these carbonizates were carried out, because use of active carbon in industrial and chemical application may be of great importance. From the results obtained, carbonization temperature seems to be the most important factor that influences the enlargement of specific surface area. Specific surface area of raw coal is 88 m²/g and in the process of carbonization becomes enlarged almost by factor 3. The same situation (enlargement of the surface area) can be observed with enlargement of particle size. Results also showed us that retention time of 60 min is the most favorable for enlargement of the specific surface area.

Introduction

Lignite, known as a high volatile coal is excavated in Velenje Coal Mine and used in Thermo Power Plant Šoštanj for electricity production. At coal combustion large amounts of gases and dust are emitted into the environment, which can cause harmful effects. Following the desire for the reduction of these impacts Velenje Coal Mine has joined the world trends in the development and application of technologies aimed at the reduction of the negative effects of production and consumption of coal. Due to lignite's low energy content, it is possible to make lignite economically and ecologically viable with its transformation to carbonizate in rotary kiln reactors.¹ The term "carbonization" means to convert to carbon, which is achieved by pyrolysis in the mentioned process, in

which thermal depolymerization of macromolecules, like cellulose, semicellulose and lignin, occur in the absence of oxygen. A solid, black residue (carbonizate), noncondensable gases and a liquid/oily phase are produced.² The carbonizate and the carbonizate briquettes can be used for household cooking and household and industrial heating. Moreover, the carbonizate can be used as active carbon in industrial and chemical applications, e.g. gas cleaning, waste and drinking water treatment and as reducing agent in metallurgical processes.

Coals and their products are highly porous materials with most of their surface area enclosed in pores with diameter of less than 50 nm. Coal porosity plays a key role in practically all aspects of its utilization: diffusion of methane and other gases from coal seams, gasification, production of metallurgical coke, activated carbon, and carbon molecular sieves.^{3,4} Thermal decomposition of carbonaceous material followed by activation with chemicals, steam or carbon dioxide at elevated temperatures are usual procedures for activated carbon production. The majority of the volatiles are removed in the form of gaseous products and a carbonized intermediate product is obtained.⁵ The activation process involves essentially the removal of tarry carbonization products formed during pyrolysis from the spaces between elementary microcrystallites, thereby opening the pores.⁶ The very large porosity provides a large surface area, which results in exceptional adsorptive properties. Therefore, activated carbons can be used as adsorbents, filters, catalyst supports, reactants and pigments and in numerous other applications.⁷

Adsorption on porous carbons was described as early as 1550 b.c. in an ancient Egyptian papyrus and later by Hippocrates and Pliny the Elder, mainly for medical purposes.⁸ The adsorptive properties of charcoal were first observed near the end of the 18th century. It was discovered that charcoal was capable of decolorizing certain liquids. This discovery led to the first industrial use of charcoal in an English sugar refinery in 1794.⁹

Since 1938, when the BET (Brunauer-Emmet-Teller) equation was developed, surface area of porous adsorbents has been determined on a routine basis from nitrogen adsorption isotherms measured at 77 K. But later the observations showed that adsorption of N₂ on coals and their products at 77 K involves activated diffusion into the internal pore structure, so it is generally accepted that this method does not measure the

total surface area of coals and their products.³ Surface areas of coals should be measured by adsorption of gases that have small molecular size and high critical temperature. CO₂ meets these criteria: it is a small molecule (0.33 nm compared to 0.365 nm for N₂ molecule), and has a critical temperature of 304.5 K. CO₂ adsorption can be used for determination of the surface area of not only anthracites, but also highly oxygenated coals, for example, lignites.^{4,10,11}

Experimental

The lignite samples were carbonized in a continuously running electric laboratory-scale rotary kiln reactor at five different temperatures (550, 600, 650, 700, 750 °C), using various particle size categories (4-10, 10-20 and 20-40 mm) and retention times (15, 30, 60 and 120 min). Laboratory tests were executed in the laboratory of the Coking, Briquetting and Thermal Waste Treatment Group, Aachen University. The scheme of the laboratory rotary kiln reactor is shown in Figure 1. The coal was charged from the bunker (left) into the kiln by a screw conveyor. At the end of the kiln (right) the carbonized coal was collected in a drum. The temperature of carbonization is controlled by the electrical heating muffle. Hydrogen, carbon monoxide, carbon dioxide and methane form the main part (in average 80 vol%) of the permanent gas, which is released from coal during the pyrolysis. As the temperature increases, a larger amount of each component is released from the coal. Released gases were piped into a burner where they burnt up completely after passing a cooling system containing a membrane pump with a vacuum controller (~20 mbar). Gases can be combusted with an adequate surplus of oxygen, producing mainly CO₂ and H₂O and in minor amounts also SO₂ and NO₂. The emissions of CO during good combustion are negligible. A later industrial size kiln can use the generated heat by burning the permanent gas as well as the condensable part of the pyrolysis gas because a separation of the components for analysis is not imperative. The heat will be more than sufficient to reach thermal autarkic operating conditions. Only for start up an external source of energy (diesel, gas, kerosene, etc) is necessary.¹² The advantages of this process are the 100 % combustion of the pyrolysis gases and the oxidation of organic sulphur compounds during the process. The final product that has a significantly higher heating value does not release any smoke or

unpleasant odours during combustion when used as fuel for household or industrial consumption.

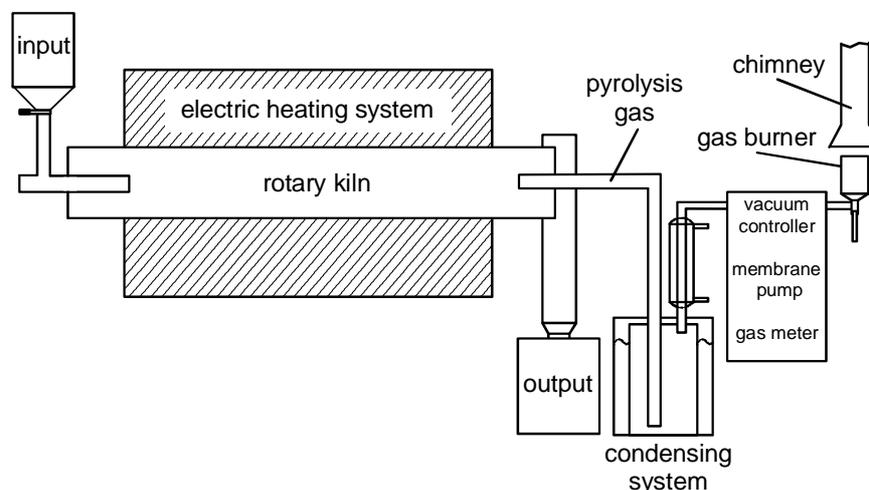


Figure 1. Scheme of the laboratory rotary kiln system.

Analytical method

Specific surface areas of the carbonizate samples were determined using a Micromeritics TriStar 3000 Analyzer. As the saturation pressure (P_0) of CO_2 at 273,15 K is 26141,72 mmHg and the pressure gauge of the analyzer can handle pressures only up to appr. 810 mmHg, the relative pressure ratio (P/P_0) is limited to the range up to appr. 0,031. Higher relative pressure ratios can only be maintained if the temperature is reduced as the saturation pressure depends on the temperature. Within the possible relative pressure ratio 8 measuring points are set of which minimum 5 points will be used for the BET-surface calculation. The exact pressure as well as the dosed CO_2 (Grade 5.0) will be measured once the adsorbed gas volume is constant in a pre-set time frame. Carbonizate samples of 0.3 g are firstly degassed at 423.15 K using a vacuum of 0.05 mbar for 90 minutes. After cooling down the analysis starts at a relative pressure ratio of 0.001. N_2 has been found inoperative for the BET-surface determination of carbonizates as the adsorption is too slow.

Results and discussion

The effects of carbonization time, carbonization temperatures and particle size of Velenje coal on quality and surface area of carbonizates are presented in next tables and

figure. The feed of coal into the laboratory rotary kiln reactor was kept constant at 2.7 kg/h for all tests. Before the tests coal was crushed and sieved to prepare three particle size categories, which had the following features:

Table 1. Particle size categories of the charged coal.

Coal		Fine fraction	Middle fraction	Coarse fraction
Particle size	[mm]	4-10	10-20	20-40
Moisture _(ad)	[wt%]	34.6	33.5	31.9
Ash _(dry)	[wt%]	17.4	18.1	20.1
Volatile matter _(daf)	[wt%]	65.4	66.1	68.0
Fixed carbon _(daf)	[wt%]	34.6	33.9	32.0
Gross calorific value _(daf)	[kJ/kg]	25810	25780	24700
Carbon _(daf)	[wt%]	66.8	66.7	63.8
Hydrogen _(daf)	[wt%]	5.45	5.56	5.62
Nitrogen _(daf)	[wt%]	1.39	1.27	1.01
Total sulphur _(dry)	[wt%]	2.63	2.33	1.82

Table 1 shows that the coal provided for the test was very inhomogeneous. However, the variations in the gross calorific value (GCV) correlate with the variations in the carbon and hydrogen contents. It seems that the ash content depends on the fraction size meaning that finer material contains less ash. This might however be a coincidence as once also an ash content of 8.9 wt%_(dry) was determined in the middle fraction category, which additionally proves the inhomogeneity of the coal.¹²

Carbonization temperature

In the first series of carbonization tests, the influence of the different temperatures was determined using coal from the middle fraction category and a retention time of 30 minutes in the heated part of the kiln. Through carbonization, the ash content of the solid material increased and volatile matter decreased. It is unusual that the increase in the ash content does not correlate with the temperature but with respect to the high variations in the ash content in the coal this was to be expected.¹² The results given in Table 2 however lead to the conclusion based on the content of carbon, hydrogen and volatile matter in carbonizates that a minimum temperature of 750 °C will be necessary to achieve a sufficient pore structure in the carbonizate, which was also confirmed by the

specific surface area determination. For the production of activated carbon, it is an advantage if the ash content in the coal is as low as possible. The total sulphur content was slightly decreased but with respect to the German¹³ and Slovene¹⁴ environmental regulations this content is still too high for the unobjectionable use in small fireplaces. Therefore, tests must be carried out to determine whether enough sulphur remains in the ash during combustion. Otherwise additives will have to be added to the briquettes to reduce sulphur emissions.

Table 2. Influence of the temperature on the carbonizate quality.

Carbonizate		550	600	650	700	750 [°C]
Moisture _(ad)	[wt%]	0.8	0.6	0.8	1.6	0.7
Ash _(dry)	[wt%]	21.7	27.7	27.2	27.4	24.7
Volatile matter _(daf)	[wt%]	25.8	19.1	14.8	11.8	9.0
Fixed carbon _(daf)	[wt%]	74.2	80.9	85.2	88.2	91.0
Gross calorific value _(daf)	[kJ/kg]	32070	33340	34120	34230	34610
Carbon _(daf)	[wt%]	84.7	89.1	91.8	94.2	96.9
Hydrogen _(daf)	[wt%]	3.67	3.13	2.68	2.09	1.65
Nitrogen _(daf)	[wt%]	1.98	2.02	2.02	1.97	1.91
Total sulphur _(dry)	[wt%]	1.94	1.52	1.92	1.81	2.17

Carbonization time

In the second series of carbonization tests, the influence of the different carbonization times was determined using coal from the middle fraction category at a temperature of 750 °C.

Table 3. Influence of the retention times on the carbonizate quality.

Carbonizate		15	30	60	120 [min]
Moisture _(ad)	[wt%]	0.9	0.7	0.8	0.6
Ash _(dry)	[wt%]	22.3	24.7	25.3	22.8
Volatile matter _(daf)	[wt%]	13.3	9.0	6.3	9.1
Fixed carbon _(daf)	[wt%]	86.7	91.0	93.7	90.9
Gross calorific value _(daf)	[kJ/kg]	33950	34610	34300	34220
Carbon _(daf)	[wt%]	92.4	96.9	97.5	95.2
Hydrogen _(daf)	[wt%]	2.52	1.65	1.47	1.83
Nitrogen _(daf)	[wt%]	1.84	1.91	1.66	1.67
Total sulphur _(dry)	[wt%]	1.66	2.17	1.90	1.85

A retention time of 60 minutes is advantageous as a low content of volatile matter and hydrogen results in high carbon content. As a carbon-matrix is necessary for activation purposes it is expected to achieve the best results if the carbonizate is to be used as active carbon. A well-controlled carbonization process can help at the enlargement of the inner surface of the grains.¹²

Particle size

In the third series of carbonization tests, the influence of different particle sizes was determined using a temperature of 750 °C and a carbonization time of 30 minutes in the heated part of the kiln.

Table 4. Influence of the particle size on the carbonizate quality.

Carbonisate		4 - 10	10 - 20	20 – 40 [mm]
Moisture _(ad)	[wt%]	0.9	0.7	1.6
Ash _(dry)	[wt%]	30.4	24.7	17.0
Volatile matter _(daf)	[wt%]	10.2	9.0	8.0
Fixed carbon _(daf)	[wt%]	89.8	91.0	92.0
Gross calorific value _(daf)	[kJ/kg]	34330	34610	34610
Carbon _(daf)	[wt%]	96.3	96.9	96.0
Hydrogen _(daf)	[wt%]	1.65	1.65	1.70
Nitrogen _(daf)	[wt%]	2.01	1.91	1.58
Total sulphur _(dry)	[wt%]	2.00	2.17	1.75

According to results the coarse fraction category has the lowest content of volatile matter (Table 4). As it can be seen from Figure 2, the decrease in hydrogen and carbon dioxide content in the released gas correlate with the increase in methane and carbon monoxide content. As bigger grains produce less hydrogen and carbon dioxide, it can be assumed that the gas phase reacts within the grain while releasing these components. It seems that the following reactions increasingly occur:



The longer contact time might cause the inner surface to grow, which was also confirmed by the specific surface area determination. If the gas phase reacts with the

solid carbon in this way, the carbonizate must go through a reduction in its mass, which could be proven.¹²

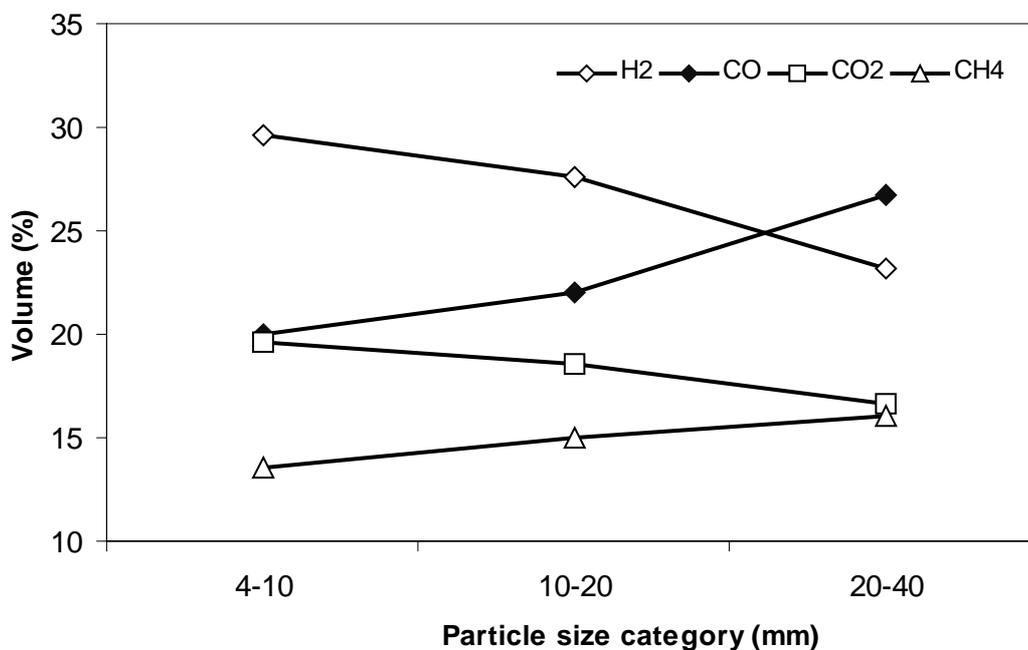


Figure 2. Influence of the particle size on the main permanent gas components.

Specific surface area determination

Specific surface area determination of raw coal and carbonizates was performed after carbonization tests. Results are presented in the next table.

Table 5. Specific surface area of coal and carbonizates.

Samples	S BET (m ² /g)				
Coal	88.2				
Carbonizates					
Temperature (30 min, 10-20 mm)	S BET (m ² /g)	Particle size (30 min, 750 °C)	S BET (m ² /g)	Carbonization time (750 °C, 10-20 mm)	S BET (m ² /g)
550 °C	156.3	4-10 mm	235.4	15 min	221.8
600 °C	179.4	10-20 mm	249.4	30 min	248.8
650 °C	195.8	20-40 mm	262.7	60 min	257.6
700 °C	213.5			120 min	249.6
750 °C	250.6				

The temperature range of carbonisation employed in the present study lied between 550 and 750 °C. Specific surface area of raw coal was 88 m²/g and in the process of carbonization was enlarged nearly for factor 3. As it can be seen in Table 5, surface area of carbonizates increase with carbonisation temperature. This had to be expected because at higher temperatures cross-links between carbonaceous aggregates break, with further rearrangement of carbonaceous aggregates and formation of new stronger linkages which cause a more porous structure.^{15,16} Higher values of the surface area are expected with coals or their products (carbonizates) with lower O/C ratios.¹⁵ Results of our study are also related to that fact, indicating that O/C ratio at 600 °C carbonizate was 0.48 and at 750 °C carbonizate was 0.31. The same situation (enlargement of the surface area of carbonizates) can be observed with enlargement of the particle size of lignite precursors. Results also showed that carbonization time of 60 min is preferable for enlargement of the specific surface area. Later on, with longer time of carbonization, the decrease of the surface area can be observed. However, this depends on the design of the kiln as longer carbonization time can only be realized if the kiln rotates more slowly. This causes an insufficient mixing respectively an insufficient heat transfer for carbonization.

For now there is no data available about pore size distribution of carbonizates, which is also important data. Therefore, mentioned determination should be done in the future. As next step also laboratory activation (physical and chemical) will be done with the purpose of enlarging the specific surface area of the produced carbonizates. Physical activation will be performed with steam and carbon dioxide, while for chemical activation different chemicals will be used as activated agents, such as phosphoric acid, zinc chloride and potassium hydroxide.

Conclusions

Production of activated carbons from coals has been of interest for years. As known, in Šalek valley, Slovenia, there are still large reserves of lignite, which can be exploited and used in economical and environmental friendly way. The results of the presented study can be significant for the development of new technologies for the wide use of lignite carbonization products.

Acknowledgements

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Povzetek

V letu 2002 je bila v rotirajočem laboratorijskem reaktorju izvedena karbonizacija pri petih različnih temperaturah (550, 600, 650, 700, 750 °C), pri štirih različnih časih zadrževanja premoga v peči (15, 30, 60 in 120 min) ter treh različnih velikosti delcev (4-10, 10-20 in 20-40 mm). Tem vzorcem smo določili specifične površine, kajti aktivno oglje se uporablja v različnih industrijskih in kemijskih aplikacijah. Rezultati kažejo, da je temperatura karbonizacije najpomembnejši faktor, ki vpliva na povečanje specifične površine. Specifična površina surovega premoga je 88 m²/g in se v procesu karbonizacije poveča skoraj za faktor 3. Z višanjem temperature raste specifična površina, enak trend pa zasledimo tudi pri večanju velikosti delcev premoga, ki ga piroliziramo. Pomemben je tudi čas zadrževanja premoga v rotacijski peči – pokazalo se je, da je najprimernejši čas zadrževanja 60 min, saj le-ta pripomore k dodatnemu povišanju vrednosti specifične površine.