

# EFFECT OF CHEMICAL ACTIVATION ON SORPTION CHARACTERISTICS OF SELECTED WOOD SAMPLES

## VLIV CHEMICKÉ AKTIVACE NA SORPČNÍ CHARAKTERISTIKY UHLÍKATÝCH MATERIÁLŮ

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### Abstract

Two samples of hardwood, beech and a mixture of beech and oak were pyrolyzed by continuous chemical activation with  $K_2CO_3$ . Two final temperatures were tested on activated samples (550 °C, 750 °C). In the same temperature regime, also non-activated original samples were pyrolyzed. The sorption for carbonaceous material was measured with a high-pressure thermal analyzer (TGA-HP50) in the presence of nitrogen and the carbon dioxide atmosphere in the range of pressure from 0,03 to 4,5 MPa, respectively from 0,03 to 2 MPa. The sorption experiments were carried out at three different temperatures – 20, 30 a 40 °C. The tests indicate that the final temperature of activation and sorption conditions (pressure, temperature) have significant impact on sorption properties of material.

### Abstrakt

Dva vzorky tvrdého dřeva, buk a směs buk/dub, byly pyrolyzovány se současnou chemickou aktivací  $K_2CO_3$ . Testovány byly dvě konečné teploty pyrolýzy pro aktivaci vzorků (550 °C, 750 °C). Ve stejném teplotním režimu byly pyrolyzovány i neaktivované původní vzorky. Sorpce na uhlíkové materiály byly měřeny na vysokotlakém termickém analyzátoru (TGA-HP50) v atmosféře dusíku a oxidu uhličitého v rozmezí tlaků od 0,03 do 4,5 MPa, respektive od 0,03 do 2 MPa. Sorpční experimenty probíhaly při třech teplotách – 20, 30 a 40 °C. Ukazuje se, že konečná teplota aktivace a sorpční podmínky (tlak, teplota), mají významný vliv na sorpční vlastnosti materiálu.

**Key words:** gas adsorption, pyrolysis, activation, activated carbon, adsorption capacity

## 1 INTRODUCTION

Various carbonaceous materials such as coal, polymers, and biomass are used for the preparation of sorbents which are the important materials for the separation of individual components of mixtures. Adsorption is a widely used process for removing dissolved solids from solutions, or for removing individual gases from gaseous mixtures. [1] The progress and results of adsorption are affected the most by porosity and the size of the surface area of the given substance. These, no doubt are determined by the origin and composition of the material. In this regard, many adsorbents were described, having different properties due to which they can be used in various industrial fields [2, 3].

Activated carbon is one of the most common and widely used adsorbents in various industrial sectors, such as the pharmaceutical industry, treatment (waste water treatment), hydrometallurgy (extraction of gold from solution), etc. It can also be used as a catalyst or as its carriers [4, 5]. The production of activated carbon consists of several processes: drying, carbonization and subsequent activation. The carbonization takes place at a low heating rate because of the higher yields of the desired solid product. The activation is achieved by improving the textural parameters [6]. Requirements for the production of activated carbon are still increasing due to the expansion of its possible use, in particular, for regulating pollutants in the environment. For this reason, the price of commercially used adsorbents based on coal or on the solid products after the distillation of crude oil, is constantly increasing. Therefore, the possibility of the substitution with new cheap materials which would be adequate substitutes for the existing ones is intensively investigated on a long-term basis [7].

Lignocellulosic material, whose main benefits are affordability, recoverability and balanced geographical distribution, may be the alternative source for the production of sorbents. Lignocellulosic biomass consists mainly of a polysaccharide component, which is represented by cellulose and hemicellulose, and of an amorphous aromatic component represented by lignin. A minor part is represented by inorganic components, such as compounds of alkali metals, sulphur, chlorine, phosphorus, etc. Cellulose, hemicellulose and lignin are the main components whose presence in biomass plays an important role in the pyrolysis process, especially in the distribution of pyrolysis products [8].

## 2 EXPERIMENTAL PART

### 2.1 Sample characterization

Two samples of wood biomass were tested which represent hard leaf wood. The samples were treated to a grain size below 3 mm. The composite sample of beech/oak comes from the firm J. Rettenmaier & Söhne GmbH + CO (Räuchergold HBK 750 – 2000) and is normally used as fuel for smoking, while beech is waste material in this case. Tab. 1 shows the basic parameters of these samples.

**Tab. 1** Gross and ultimate analysis of wood biomass

Parameters (% wt. on dry basis)	Beech	Beech/Oak
Moisture	0,0	0,0
Total combustible matter	99,5	99,0
Volatile content	83,3	82,7
Ash	0,5	1,0
Heat of combustion (MJ/kg)	19,1	19,4
Calorific value (MJ/kg)	17,7	18,1
Carbon content	48,6	48,6
Hydrogen content	6,3	6,0
Nitrogen content	0,1	0,2
Oxygen content	44,5	44,2
Sulphur content*	0,0	0,0
Chlorine content	< 0,01	0,0
Fluorine content	ND	0,0
Bromine content	ND	0,0

\* Sulphur content in total

ND - not determined

### 2.2 Pyrolysis and chemical activation

The samples of biomass, beech and the mixture of beech and oak were activated with a 41.18% potassium carbonate solution in a ratio of 3:1 ( $K_2CO_3$ : sample). The sample and the reagent were first weighed in the given proportions and thoroughly mixed in a mortar all the biomass to be impregnated. Since the samples were of a different particle size, the resulting suspension was of different consistency. The treated samples were left for 24 hours in sealed plastic sample containers at room temperature. Subsequent drying was then carried out for 24 hours at a temperature of 105 °C. After drying, the samples had to be mashed in the mortar. The prepared samples were pyrolyzed in two temperature regimes. For comparison, raw biomass without prior impregnation was pyrolyzed in the same manner.

The pyrolysis was carried out in a tubular retort made of corundum, through-going at both ends due to the continuous supply of nitrogen. The retort, stored in a horizontal electrically heated furnace, was heated at a rate of 10 °C/min to a temperature of 550 °C, and 750 °C respectively. The residence time at the final temperature was 60 minutes, and during the experiment, nitrogen was continuously fed at a flow rate of 100 ml/min. The obtained activated samples were washed several times with hot distilled water stirring continuously and for the residence time at the boiling temperature of 15 minutes. The pH value was continuously measured. When reaching a neutral pH value, the samples were washed with cold distilled water. Finally, the drying was carried out at a temperature of 105 °C for 24 hours. In total, eight solid products were obtained, which are listed in Tab. 2.

**Tab. 2** Indication of derived pyrolysis products

Sample	<u>activated</u>		<u>non-activated</u>	
	550 °C	750 °C	550 °C	750 °C
Beech	Beech_550_A	Beech_750_A	Beech_550_NA	Beech_750_NA
Beech/Oak mix	Beech/Oak_550_A	Beech/Oak_750_A	Beech/Oak_550_NA	Beech/Oak_750_NA

### 2.3 Adsorption on solid pyrolysis products

The sorption tests were conducted on the special TGA HP50 device which is designed to provide the most accurate information about the change in sample weight with a change in temperature, pressure, atmosphere, and time. The experiments were carried out in the nitrogen atmosphere at a pressure ranging from 0.03 to 4.5 MPa in order to monitor the dependence of the sorption ability of the material on the increasing pressure. The beech sample was also tested in the carbon dioxide atmosphere at a pressure ranging from 0.03 to 2 MPa in order to monitor the adsorption on the prepared material. The settings of the sorption experiments were as follows: Each test consisted of four series which took place at temperatures of 20, 30 and 40 °C. The first three series were carried out in the presence of nitrogen or carbon dioxide. The last series was carried out in the presence of helium and was included for the reason of performing the correction for buoyancy. Each series then consisted of 14 steps at pressures ranging from 0.03 to 4.5 MPa in the nitrogen atmosphere, and from 0.03 to 2.7 MPa in the helium atmosphere, and from 0.03 to 2 MPa in the carbon dioxide atmosphere. Before each experiment, the sample was dried at 110 °C for 3 hours and evacuated, thereby ensuring degassing the sample. The initial sample weighted portion was 35 mg for the activated samples and 50 mg for the non-activated samples. The difference in the weighed portions is due to the specific density of the activated and non-activated samples. The limiting factor is the size of the pot. The test result is the dependence of the amount of adsorbed gas on pressure and temperature. The textural properties of raw biomass and its pyrolysis products were determined using the  $S_{\text{BET}}$  physical adsorption of nitrogen at -196 °C.

## 3 RESULTS AND DISCUSSION

The resulting data of sorption experiments reflect the dependence of the test material on temperature, pressure and time which determines the length of each step. The measurement in the presence of helium was included due to the correction for buoyancy, which is required when using such a pressure range [9]. With the increasing pressure, also the density of adsorbed gas changes significantly, and thus it is necessary to know the compressibility factor and the volume of the pot. The results of the individual tests, representing the amount of adsorbed gas at maximum achieved pressures, are expressed in percentage by weight (by the weight of clean adsorbent) and are shown in Tab. 3 and Tab. 4. Tab. 5 presents the textural parameters of each sample which were extracted by physical adsorption of nitrogen. The analyses were performed at a temperature of -196 °C using the ASAP 2020 device (Micromeritics, USA). Before the measurement, the samples were treated for 24 hours at a temperature of 105 °C and a vacuum below 1 mbar. The specific surface area  $S_{\text{BET}}$  was evaluated from the adsorption isotherm of nitrogen by means of the standard Brunauer–Emmett–Teller (BET) procedure [10, 11] at a pressure range  $p/p_0 =$  from 0.05 to 0.25. The surface of mesopores  $S_{\text{meso}}$  and the volume of micropores  $V_{\text{mikro}}$  was determined using the method from the t-graph [12]. The total pore volume  $V_{\text{total}}$ , was determined from the adsorption isotherm of nitrogen at a maximum pressure of  $p/p_0$  (~ 0.994). The pore size distribution was calculated from the adsorption branch of the adsorption-desorption experiment with nitrogen using the method Barrett–Joyner–Halenda (BJH) [13] when the Roberts process [14] was used assuming cylindrical pore geometry. The Lecloux–Pirard standard isotherm with the constant  $C_{\text{modif}}$  [15, 16] was used for both the construction of the t-graph and the evaluation of the pore size distribution.

**Tab. 3** Results of sorption tests in the environment of N<sub>2</sub> at a pressure of 4.5 MPa

Adsorbent amount of N <sub>2</sub> (wt.%)	<b>Beech</b>			
	Beech_550_NA	Beech_750_NA	Beech_550_A	Beech_750_A
T=20 °C	5,69	7,32	7,13	13,94
T=30 °C	5,59	6,48	6,78	12,12
T=40 °C	5,67	6,45	7,37	12,07
Adsorbent amount of N <sub>2</sub> (wt.%)	<b>Beech/Oak</b>			
	Beech/Oak_550_NA	Beech/Oak_750_NA	Beech/Oak_550_A	Beech/Oak_750_A
T=20 °C	4,29	5,57	4,96	10,65
T=30 °C	4,36	5,76	6,32	10,86
T=40 °C	4,46	5,86	6,62	9,88

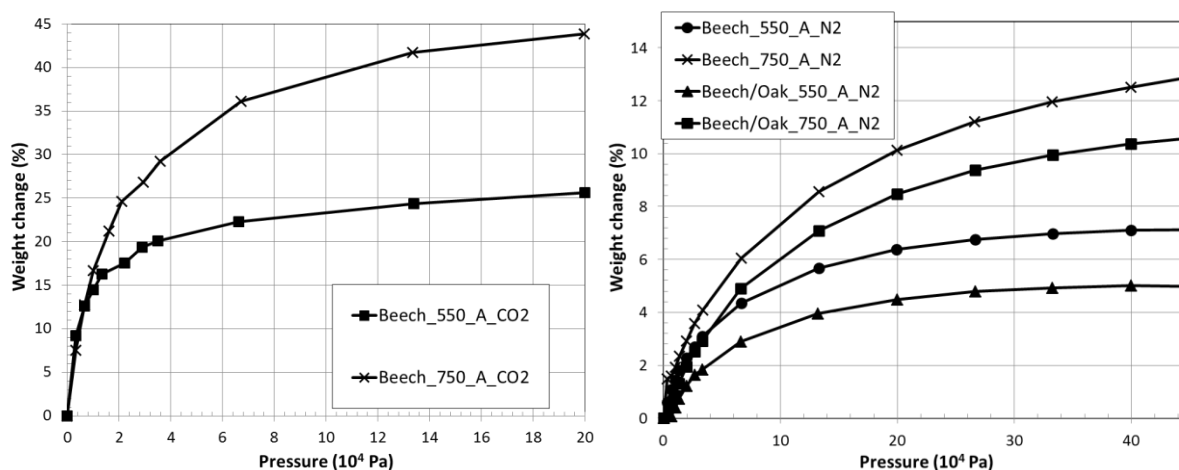
**Tab. 4** Results of sorption tests in the environment of CO<sub>2</sub> at a pressure of 2 MPa

Adsorbent amount of CO <sub>2</sub> (wt.%)	<b>Beech</b>			
	Beech_550_NA	Beech_750_NA	Beech_550_A	Beech_750_A
T=20 °C	14,33	18,99	25,59	43,85
T=30 °C	13,68	16,76	24,55	41,78
T=40 °C	13,52	16,12	24,59	39,45

**Tab. 5** Characteristic sorption parameters of pyrolytic carbons

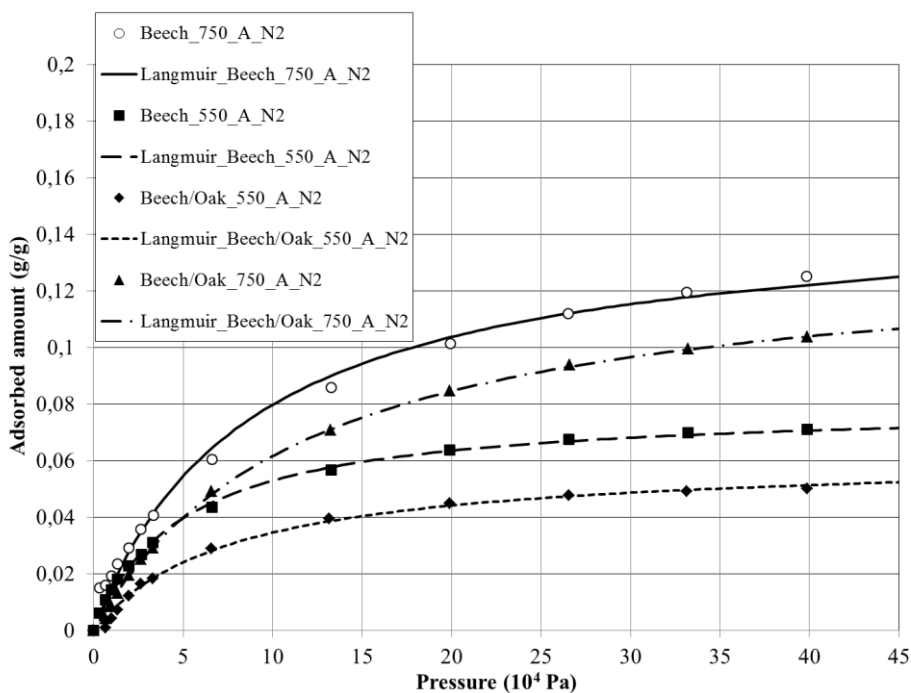
Sample	S <sub>BET</sub> (m <sup>2</sup> /g)	S <sub>meso</sub> (m <sup>2</sup> /g)	V <sub>micro</sub> (mm <sup>3</sup> <sub>liq</sub> /g)	V <sub>total</sub> (mm <sup>3</sup> <sub>liq</sub> /g)	V <sub>micro</sub> /V <sub>total</sub> (%)	C <sub>modif</sub> (-)
Beech	4,08	-	-	-	-	-
Beech_550_NA	382,6	53,8	154	179	86	29,1
Beech_750_NA	140,4	12	64	72	89	21,5
Beech_550_A	548,2	43,7	247	273	90	24,3
Beech_750_A	1097,3	132,9	456	532	86	27,2
Beech/Oak	0,16	-	-	-	-	-
Beech/Oak_550_NA	222	27,4	96	114	84	22,8
Beech/Oak_750_NA	5,2	1	2	3	67	22
Beech/Oak_550_A	380	41,6	166	195	85	25
Beech/Oak_750_A	951,4	94,3	399	459	87	29,8

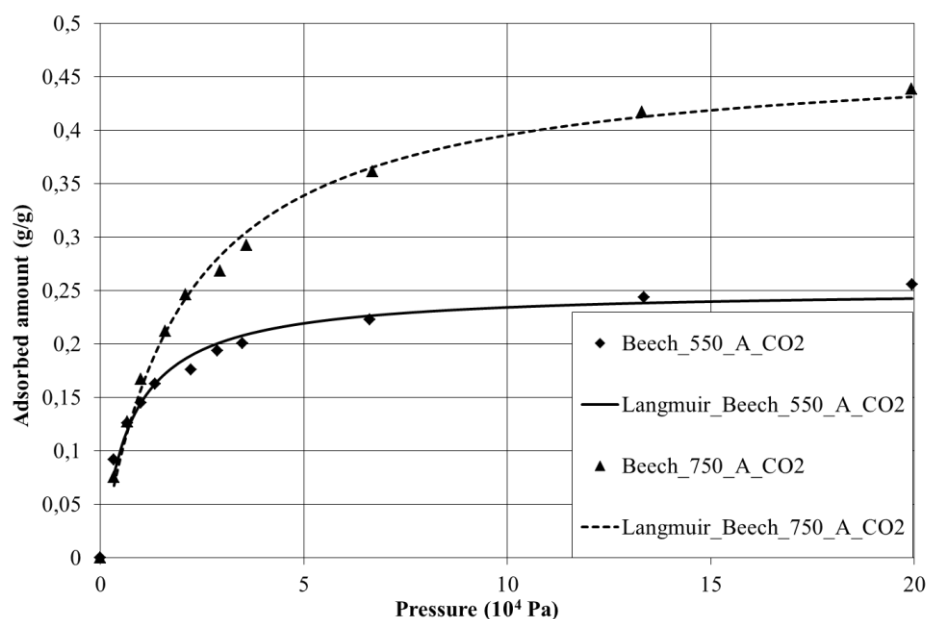
It is obvious that the temperature of activation and the origin of sample have a great influence on the sorption properties. As shown, the final pyrolysis temperature of 750 °C has a clearly better effect on the adsorption abilities of the activated material. The best results were obtained for a beech sample activated at a temperature of 750 °C where 13,94 % of nitrogen was adsorbed at a pressure of 4.5 MPa and a temperature of 20 °C. The results of sorption experiments are in correlation with the values obtained by the BET method of nitrogen adsorption at a temperature of -196 °C. Based on the obtained results of adsorption tests taking place in the atmosphere of nitrogen, further sorption experiments were carried out in the CO<sub>2</sub> environment on a sample of beech. The courses of adsorption isotherms for activated samples are shown in Fig. 1.



**Fig. 1** Adsorption isotherms of activated samples in the CO<sub>2</sub> and N<sub>2</sub> atmospheres at a temperature of 20 °C

The pressure in the sorption experiments revealed clearly, in particular the higher the pressure, the higher the amount of adsorbed gas. From the behaviour of adsorption isotherms, a surge in the amount of adsorbed nitrogen is evident up to a pressure of 1.3 MPa. On the contrary, for carbon dioxide, the most pronounced effect of the pressure up to 0.6 MPa was observed. A further increase in pressure for CO<sub>2</sub> causes an increase in the adsorbed amount by 18 % only as for the sample Beech\_750\_A, resp. by 13 % as for the sample Oak\_550\_A. The Langmuir isotherm (see Fig. 2) was fitted in a basic shape to the obtained data by the method of minimizing  $\chi^2$ . For the adsorption of CO<sub>2</sub>, the surface area for both samples of activated beech was calculated based on the parameters of the Langmuir isotherm. The value for beech activated at 550 °C is 643 m<sup>2</sup>.g<sup>-1</sup> ( $S_{\text{BET}}$  548 m<sup>2</sup>.g<sup>-1</sup>), the value for beech activated at 750 °C is 1214 m<sup>2</sup>.g<sup>-1</sup> ( $S_{\text{BET}}$  1097 m<sup>2</sup>.g<sup>-1</sup>). Both variations can be explained by the different methodologies as well as by the different nature of the used adsorptives. The measured results are in accordance with generally accepted regularities of adsorption which are described in the literature.





**Fig. 2** Langmuir isotherms of activated samples at 20 °C in the N<sub>2</sub> and CO<sub>2</sub> environments

#### 4 CONCLUSIONS

The sorption properties of two different samples of biomass were tested using the high thermal analyzer TGA HP50. Nitrogen and carbon dioxide were adsorbed chemically by activated pyrolytic carbons in environments of different pressures and temperatures. It is evident that the sample Beech activated at a temperature of 750 °C showed the best sorption abilities, in particular during the sorption of both nitrogen and carbon dioxide where the maximum adsorbed amount of CO<sub>2</sub> reached approximately 44 % (sample Beech\_750\_A ). These results are consistent with the textural parameters of carbons obtained by the physical adsorption of nitrogen using another apparatus.

The dependence of the adsorbed amount of the tested gases on their pressures was experimentally confirmed in accordance with the general technical awareness (the higher the pressure, the greater the amount is absorbed). The high thermal analyzer TGA - HP50 is thus proved itself to be a suitable instrument for this type of experiment. The dependence of the adsorbed gas amount on the pressures is more significant up to the pressure of 1.3 MPa (N<sub>2</sub>) or 0.6 MPa (CO<sub>2</sub>). Further increasing the pressure makes the progress of sorption more gradual. The effect of temperature on the amount of adsorbed gas was observed as well. The lowest temperature of 20 °C of the three tested temperatures is suitable the most.

The performed experiments showed that the obtained results may be useful for the design of equipment intended for dividing gas mixtures, thus other biomass samples will be further tested and measurements with another major greenhouse gas – methane – will be included as well.

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## RESUMÉ

Dva vzorky byly pyrolyzovány a současně aktivovány uhličitánem draselným při dvou různých konečných teplotách pyrolýzy (550 a 750 °C). Pyrolyzovány byly rovněž vzorky bez předchozí aktivace. Osm takto získaných pevných uhlikatých produktů bylo po předchozí úpravě testováno na přístroji TGA-HP50 za účelem zjištění sorpčních vlastností těchto materiálů. Sorpční testy probíhaly při třech teplotách (20, 30 a 40 °C), v prostředí dusíku a oxidu uhličitého. V průběhu experimentů byl zvyšován tlak plynu, a to od 0,03 do 4,5 MPa v prostředí N<sub>2</sub> a od 0,03 do 2 MPa v prostředí CO<sub>2</sub>. Vysoký potenciál biomasy pro výrobu aktivovaných pyrolýzních uhlíků byl v této práci potvrzen. Chemicky aktivované vzorky vykazovaly lepší výsledky než vzorky neaktivované. S vyšší teplotou pyrolýzy se sorpční schopnosti aktivovaného materiálu zlepšovaly. Výsledky dokazují, že z dřevní biomasy lze vyrobit materiál s velkým povrchem, který může být následně použit jako sorbent s výraznou selektivitou k CO<sub>2</sub>.