

Thermochemical Conversion of Bean Pods to Carbon Materials and Gas

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ABSTRACT

The preparation of activated carbons from bean pods by chemical (K_2CO_3) and physical (water vapor) activation was investigated. The carbon prepared by chemical activation presented more developed porous structure than one obtained by water vapor activation. Carbon adsorbent with very low ash content and developed micropore structure is obtained by thermochemical treatment with conc. H_2SO_4 of liquid products from carbonization of bean pods and activation with water vapour.

Key words: bean pods, K_2CO_3 activation, water vapor activation

1. INTRODUCTION

It has been suggested recently by many scientists that in the future the use of biomass of forestry origin will increase as a source of energy, mainly as gas and liquid products. The thermochemical conversion of agricultural by-products has received an enormous amount of attention as a consequence of its availability and its potential to produce energy as well as activated carbons with good adsorption properties. The pyrolysis of agricultural wastes is an important step in their thermal conversion, since it determines the split between char, tar and gas [1-4]. The carbonaceous char

turns out to be a good precursor for the preparation of activated carbons. The identified compounds in the carbonization liquid products are predominantly oxygen derivatives of phenol, dihydroxybenzenes, guaiacyl, syringol, vanillin, veratrol, furan, acids. Liquids with such composition are promising as raw materials for production of synthetic adsorbents (independently or with additives) and other carbon materials [5]. To the best knowledge of the authors, bean pods had not been on focus of scientific investigation for their effective utilization. Due to the unsuitable shape of the carbonized pods their contact with activation reagent (water vapour) is hindered what cause difficulties in the preparation of activated carbon with well developed structure.

The aim of this study is investigation of the possibilities for conversion of bean pods to carbon adsorbents with different properties using various thermo-chemical treatments.

2. EXPERIMENTAL

2.1. Materials

The chemical composition (organic matter fractions) of the bean pods precursor was analyzed according to the procedure of Adani [6]. Briefly, a wet-chemical method was used, yielding four fractions: soluble in a toluene-ethanol mixture, soluble in 0.94 mol dm^{-3}

sulfuric acid, soluble in 13.5 mol dm⁻³ sulfuric acid and insoluble in 13.5 mol dm⁻³ sulfuric acid. Lipids were solubilized by the first extraction step, proteins and hemicellulose by the second step, and cellulose by the third step. The lignin was left in the residual fraction.

2.2. Activation with water vapour

Bean pods were carbonized as 50 g of the raw material (fraction of 1-5 mm) was heated in a laboratory installation at atmospheric pressure and heating rate of 60°C min⁻¹ up to a carbonization temperature of 600°C. The sample was maintained at the final temperature for 10 min, and then cooled down to ambient temperature. After that the solid product was activated at 700°C with water vapour for 1 h. This sample of activated carbon is denoted as "Carbon A".

2.3. Chemical activation with K₂CO₃

The initial material of bean pods was ground down to 0.5 mm particle size. The activation process involved mixing of the initial material and the activating agent in water, in a reagent to bean pods material ratio of 2:3. The mixing was performed at room temperature under stirring for 12 h. After mixing, the slurry was subjected to drying at 110°C overnight. The chemically-loaded sample was then carbonized in a N₂ atmosphere. Carbonization was carried out by heating the sample from room temperature up to 950°C, and then maintained at this temperature for 10 min. After cooling under N₂ atmosphere, the carbonized product was washed to remove the residual chemicals. The final product was then dried at 110°C and then denoted as "Carbon B".

2.4. Preparation of carbon adsorbents from bean pods carbonization liquid products

For preparation of activated carbon with very low ash content, 100 g of bean pods pyrolysis tar is treated with H₂SO₄ at 160°C until solidification. The solid product obtained is heated up to 600°C under nitrogen atmosphere and after that activated with water vapour at 800°C. This sample of activated carbon is denoted as "Carbon C".

2.5. Characterization of porous texture

Textural characterization was carried out by measuring the N₂ adsorption isotherms at 77 K in an automatic apparatus (Micrometrics ASAP 2010 M). Before the experiments, the samples were outgassed under vacuum at 300°C overnight. The isotherms were used to calculate specific surface area S_{BET}, total pore volume V_T, and micropore volume W₀, using the DR equation [7]. The mean pore size L was evaluated from the Stoeckli-Ballerini equation, as $L = 10.8 / (E_0 - 11.4)$. The micropore surface area S_{mic} was evaluated according to the equation $S_{mic} = 2 W_0 / L$.

2.6. Oxygen functional groups

The content of oxygen-containing functional groups with acidic character on the carbon surface was determined applying the Boehm method by neutralization with bases of increasing strength: NaHCO₃, Na₂CO₃, NaOH and sodium ethoxide [8]. About 0.5 g (± 0.0001 g) of the carbon was put in contact with 100 cm³ of 0.05 N base solution in sealed flasks. The suspensions were shaken at least 16 h, and then filtered. The excess of base remaining in the solution was determined from back-titration after adding an excess of standard HCl solution. It was assumed that NaHCO₃ was capable of neutralizing all carboxylic groups, Na₂CO₃ - carboxylic and lactonic groups, NaOH - carboxylic, lactonic and phenolic groups, and sodium ethoxide was assumed to neutralize all acidic groups. The total number of basic sites was determined with 0.05 N HCl [9]. The procedure is the same as above mentioned, as back-titration of the excess of HCl was performed using titration with 0.05 N NaOH solution.

2.7. pH measurements

The pH of the carbons was measured according to the following procedure: Exactly 4.0 g of carbon was weighed into a 250 cm³ beaker, and 100 cm³ of water was added. The beaker was covered with a watch glass, and the mixture was boiled for 5 min. The suspension was set aside, and the supernatant liquid was poured off as hot as possible but not below 60°C. The decanted portion was cooled down to ambient temperature and its pH was measured to the nearest 0.1 pH unit [10,11].

2.8. Point of zero charge (PZC)

The nature of the carbon surface was determined from the pH value corresponding to the point of zero charge (PZC). This was measured by the mass titration method as described by Noh and Schwarz [12], employing the following procedure. Briefly, the activated carbon was dispersed in a suitable volume of distilled water and the suspension was subjected to constant stirring under a nitrogen atmosphere at room temperature until equilibrium was attained (ca. 48 h). Typical activated carbon/water ratios used were 1, 2, 4, 6, 8, 10, 12, 14 and 16. Once equilibrium had been reached, the pH value was measured using a glass electrode. Newly portion of distilled water was then added in order to obtain the next solid/weight fraction. The plateau in the plot of equilibrium pH versus solid weight fraction corresponded to the PZC value of the activated carbon.

3. RESULTS AND DISCUSSION

3.1. Chemical composition of the raw material

The bean pods used as carbon precursor contained a relatively high volatile matter (ca. 80 wt. %), this suggests that the carbonized matter will not present a high carbon yield after pyrolysis (12 wt. %). However bean pods are cheap, easy to handle and largely available waste. Bean pods waste is different from other wood or other lignocellulosic materials. The typical composition is 33 % cellulose, 45.6 % hemi-cellulose, 17 % lignin and a small amount of lipids (4.47 wt %). Moreover, the elemental analysis shows a low ash content and a relatively high oxygen content (almost 50 wt. %). Previous studies, carried out in our research group, have shown that the composition of agricultural by-products has strong influence on the porous and chemical features of the solid products, obtained from pyrolysis and activation [2]. It was found that high content of lignin favor the development of a macroporous structure, whereas a cellulose yields predominantly microporous materials. Bean pods exhibit a combination of large quantities of cellulose and lignin, which makes this material an appropriate candidate for preparation of carbons with developed micro- and macroporosity.

3.2. Material balance of the thermochemical conversion process of bean pods.

The material balance (Table 1) under atmospheric pressure for bean pods indicates that one half of the organic substance passes in the liquid products. The rest half of the organic matter divides equally between activated carbon and gas.

Table 1

Material balance of atmospheric pressure pyrolysis in the presence of water vapor of bean pods

Sample	Solid product, (% yield)	Liquid product, (% yield)	Gas (% yield)
Bean pods	22.8	56.4	20.8

3.3. Characterization of the adsorbents.

The chemical composition of the raw material and the solid residual products prepared from it is presented in Table 2.

Activated carbon, obtained from bean pods by physical activation with water vapour (carbon A), has relatively high ash content, and relatively high amount of oxygen. Comparatively, carbon B obtained by chemical activation with K_2CO_3 , presents a lower amount of oxygen than the carbon obtained by pyrolysis in the presence of water vapour.

In addition, the ash content in B sample is 2 times lower than typical values reported in the literature [13]. Probably this trend may be due to partial removal of mineral matter by reaction with the potassium carbonate, used as activating agent. Higher content of sulphur in the carbon C could be explained with the use of H_2SO_4 in the process of its production.

The large amount of oxygen for Carbon A and C shows that some oxygen atoms are incorporated in the carbonaceous matrix during pyrolysis and/or activation, either at the edges of the basal planes, or to the basal planes of the carbon, giving rise to different surface functionalities.

Table 2

Proximate and ultimate analysis [wt. %] of the raw precursor (bean pods) and the activated carbons obtained by different activation procedures

	Proximate analysis		Ultimate analysis				
	Ash ^d	Volatiles ^{daf}	C ^{daf}	H ^{daf}	N ^{daf}	S ^{daf}	O ^{daf}
Raw material	6.1	80.07	43.25	5.98	0.92	0.11	49.74
Carbon A	22.8	30.26	60.25	3.90	0.73	0.16	34.96
Carbon B	10.8	BDL	87.74	1.51	0.52	0.10	14.17
Carbon C	0.7	22.56	64.36	3.82	0.61	0.70	30.51

d – dry basis; daf – dry and ash free basis; BDL – below detection limit

Table 3

Textural parameters of the activated carbons, evaluated from the DR method applied to the N₂ adsorption isotherms at 77 K. For comparison purposes, data of several activated carbons from literature have also been compiled

Sample	References	S _{BET} [m ² g ⁻¹]	C _{BET}	V _{TOTAL} [cm ³ g ⁻¹]	DR method			
					W ₀ [cm ³ g ⁻¹]	E ₀ [kJmol ⁻¹]	L [nm]	S _{mic} [m ² g ⁻¹]
Carbon A	This work	258	637	0.206	0.107	16.84	1.99	100
Carbon B	This work	1580	341	0.809	0.649	18.75	1.47	830
Carbon C	This work	1210	378	0.720	0.582	17.74	1.52	596
Modified commercial activated carbons								
SB	/14/	1156	249	0.646	0.429	18.64	1.49	576
SBS	/14/	1048	256	0.559	0.388	19.28	1.37	566

Table 4

pH, point of zero charge and quantification of the oxygen-containing surface groups evaluated by the Boehm method and expressed in terms of [meq g⁻¹]

	pH	PZC	Acidic groups				Total basic
			Carboxyl	Lactonic	Hydroxyl	Carbonyl	
Carbon A	10.7	11.90	BDL	BDL	0.21	1.52	7.40
Carbon B	8.2	9.21	BDL	BDL	0.53	2.37	1.38
Carbon C	9.1	10.0	0.1	0.2	0.32	1.72	6.4

The shape and texture of the bean pods particles are not appropriate for effective activation with water vapour and CO₂, due to difficulties in interaction of

contacting surfaces of material particles with activating reagent. That is why the production of carbon adsorbents with high surface area from this material is

not an easy task. Detailed characteristics of the pore structure of the prepared carbons are summarized in **Table 3**.

Analysis of the nitrogen adsorption data using several equations indicates, that chemical activation brings about a large apparent surface area S_{BET} and large micropore volume, as opposed to steam pyrolysis (carbon A). Moreover, the average pore width L , evaluated from the Stoeckli-Ballerini equation, confirms that carbon A possesses larger pores. This is in good agreement with earlier results on the development of macroporosity from lignin-enriched biomass precursors [15]. Detailed analysis of the obtained data allow us to suggest the possibility of pore opening during chemical activation, attributed to the gasification of the samples, as a consequence of the chemical reactions between the carbon matrix, the gases desorbed upon heating (i.e. volatile matter and other gases arising from the decomposition of the surface functionalities) and the activating agent (Carbon B). It may be inferred that the final porous features of activated carbons, obtained from agricultural by-products depend not only on the composition of the precursors, but on the activation procedure also. In this sense, chemical activation favors the development of microporosity, whereas steam activation brings about pores of larger size. Data in Table 3 show that the carbon adsorbent obtained from pyrolysis of liquid products possesses very low ash content and high surface area (Carbon C). The carbon prepared by chemical activation presented more developed porous structure and considerably higher surface area than one obtained by water vapor activation.

The identification and quantification of the oxygen groups present in the prepared carbons is shown in **Table 4**.

Despite the large amount of oxygen, the values of PZC revealed that the surface groups are predominantly of basic nature. Acidic groups (carboxylic or lactone-like binding structures) have not been detected by Boehm titration, whereas phenolic hydroxyl and carbonyl groups were present in both carbons (Carbon A and Carbon B). The amount of basic groups is nearly six times higher for carbon A, which is in good agreement with the PZC values. Such basic functionalities could be due to the presence of oxygen

containing groups of basic nature or related to species in the inorganic matter of this carbon sample (which accounts for more than 30 wt. %)

4. CONCLUSIONS

Due to the unfit shape and texture of bean pods, which do not allow a good contact with the activation reagent, activated carbon obtained by activation with water vapour possesses not very high surface area. The carbon prepared by chemical activation presented more developed porous structure than one obtained by water vapor activation. Carbon adsorbent with very low ash content and well developed pore structure is obtained by conversion of liquid products from carbonization treatment of bean pods to the solid product, and its consecutive carbonization and activation with water vapor.

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