Biomass conversion to carbon adsorbents and gas

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Abstract

A process is created for the utilization of biomass by producing carbon adsorbents and gas. Carbon adsorbents with alkaline character of the surface, tar and gas products are obtained by steam pyrolysis of biomass (almond shells, nut shells, apricot stones, cherry stones, grape seeds). Mixtures of tar obtained during this process and furfural are used for obtaining carbon adsorbents with low ash and sulphur contents and different chemical character of the surface. The chemical character of oxygen functional groups on their surface reveals that they are polyfunctional cationites. Carbon adsorbents obtained have a hydrophilic surface and are suitable for removing metal ions and other pollutants from water. The gas products can be used as energy source. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

At present, agricultural by-products are mainly used as combustion feedstocks. There are, however, alternative utilization processes to convert agricultural by-products into solid, liquid and gaseous products for a more efficient exploitation of these materials [1]. Agricultural by-products have proved to be promising raw materials for the production of activated carbons because of their availability at a low price. They were used for the production of activated carbon with a high adsorption capacity, considerable

mechanical strength, and low ash content [2–8]. The carbon adsorbents can be applied for the removal of trihalomethanes and metal ions from water, purification of waste solutions, separation and concentration of traces of elements and radioactive isotopes, production and analysis of high purity substances etc. [9–11]. One of the disadvantages of activated carbon is its relatively high cost. The main reason for this is the high expense of energy indispensable for its production. A simple one-step method for the production of activated carbons has been developed [12] to reduce the energy expenditure during the process. This method is a feasible alternative to the traditional two-stage process for the production of activated carbons by consecutive carbonization of the raw material and high temperature activation (900–1000°C) of the solid product from carbonization. Agricultural

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by-products (almond shells, nut shells, apricot stones, cherry stones and grape seeds) were subjected to steam pyrolysis-activation at treatment temperatures of 600–700°C [13]. The presence of water vapour during pyrolysis leads to a considerable increase in the liquid and gas product yields in addition to reducing the sulphur content in liquid and solid products. It was established that the properties of carbon adsorbents obtained by steam pyrolysis of agricultural by-products depend on the treatment conditions (the final temperature of treatment, duration of the treatment at the final temperature) and the choice of raw materials.

The general objective of this work is, on the basis of earlier and present investigations, to create a technology for the effective utilization of biomass by producing carbon adsorbents with different surface properties and gas products.

2. Materials and methods

2.1. Activated carbon preparation

2.1.1. Preparation of activated carbon from biomass
The activated carbons have been prepared by one-step pyrolysis of almond shells, nut shells, apricot stones, cherry stones and grape seeds, in the presence of steam. Hundred grams each of the raw materials are heated in a laboratory installation in a flow of pure water vapour (120 ml/min) with a heating rate of 15°C/min to a final carbonization temperature of 800°C. In order to reduce the duration of treatment at the final temperature the temperature value is increased in comparison with temperatures used in our earlier investigations [13]. The duration of treatment at the final temperature is 1 h. After the treatment the samples are left to cool down. In order to obtain the carbons with steady content of surface oxides the steam flow is interrupted at a temperature of 300°C. The carbon particles preserve the shapes of the raw materials particles. Thus, the activated carbons have regularly formed particles.

2.1.2. Preparation of carbon adsorbents from biomass products
200 g of the following mixtures of tar from steam pyrolysis of apricot stones (TSPAS) and furfural—90 : 10, 70 : 30, 50 : 50, 30 : 70% are treated with

different amounts of H_2SO_4 (3%, 5% and 7%) and the mixture is heated to 160°C with continuous stirring. It was determined that the optimum amount of added H_2SO_4 is 5%. The solid products obtained are heated to 600°C in a covered silica crucible with a heating rate of 10°C/min under nitrogen.

Oxidation of carbonizates with air at 400°C is used to obtain activated carbon with acidic surface properties. The oxidation of samples with particle size 0.2–1 mm is performed by thermal treatment at 400°C in a horizontal tube furnace in a stream of air (8 l/h).

Steam activation with water vapour at 800°C for 1 h is used to obtain activated carbon with alkaline surface.

2.2. Porous structure analyses

The porous structure of carbon adsorbents was studied by N_2 adsorption at 77 K. The N_2 surface area and mesopore size distribution were determined using the BET equation [14] and a procedure developed by Barret et al. [15] in which the apparent pore radius was calculated by the Kelvin equation [16]. The total pore volume (V_{total}) is derived from the amount of N_2 adsorbed at a relative pressure 0.95, assuming that the pores are then filled with liquid adsorbate. The Dubinin–Radushkevich equation was used to calculate the micropore volume (V_{micro}) [17]. The mesopore volume was calculated by subtracting V_{micro} from V_{total} ($V_{meso} = V_{total} - V_{micro}$). The volume of macropores (pore size larger than 50 nm) was deduced from mercury porosometry (Carlo Erba 200).

2.3. Oxygen functional groups content

The oxygen functional groups content with increasing acidity was determined by Boehm's method [18] of titration with basic solutions of different base strengths ($NaHCO_3$, Na_2CO_3, $NaOH$, C_2H_5ONa). The basic group contents of the oxidized samples are determined with 0.05 N HCl [19].

2.4. pH determination

The procedure is as follows: 4.0 g of carbon (ground, undried) is weighed into a 250 ml beaker and 100 ml of water is added. The beaker is covered with a watch glass and heated to boiling temperature

Table 1
Chemical composition of the raw materials and the solid products

Raw materials and solid products	Proximate analysis (wt%)			Elemental analysis (wt%, maf)				
	W	Ash	Vol	C	H	N	S	O
Apricot stones	6.4	0.2	80.6	51.5	6.3	0.2	0.1	41.9
Product	1.6	2.0	3.7	89.5	2.4	0.9	0.8	6.4
Cherry stones	6.0	0.9	82.0	53.9	7.1	0.3	0.3	38.4
Product	1.6	4.2	10.0	84.0	2.2	1.0	0.4	12.4
Grape seeds	7.6	2.5	75.3	55.4	7.0	1.5	0.2	35.9
Product	1.8	13.1	4.4	84.7	1.3	1.6	0.3	12.1
Almond shells	8.7	2.3	79.7	54.7	7.5	0.3	0.3	37.4
Product	1.8	2.8	4.9	87.9	2.5	1.1	0.5	7.8
Nut shells	6.7	3.8	84.1	53.6	7.5	0.3	0.3	38.3
Product	2.1	4.9	3.4	85.9	2.1	0.5	0.5	11.0

Table 2
Yield and adsorption properties of activated carbons obtained by steam pyrolysis of agricultural by-products

Raw material	Yield (wt%)	Surface area (m^2/g)	pH	Adsorption (mg/g)	
				Iodine	Methylene blue
Apricot stones	18.2	1190	9.6	925	316
Cherry stones	11.2	875	10.1	922	235
Grape seeds	26.2	497	9.6	586	183
Almond shells	17.8	998	9.9	933	261
Nut shells	17.9	743	9.9	758	222

for 5 min. The mixture is set aside and the supernatant liquid is poured off at 60°C. The decanted portion is cooled to room temperature and is measured to approximately 0.01 pH.

3. Results and discussion

3.1. Carbon adsorbents from agricultural by-products

The chemical compositions of the carbon adsorbents obtained from different agricultural by-products are presented in Table 1. Activated carbons from almond shell, nut shell, apricot and cherry stones have low ash content. All samples have low sulphur content. The carbon from grape seeds has relatively high ash content. The carbons obtained from apricot stones and almond shells have higher carbon content and lower oxygen content than carbons obtained from cherry stones and grape seeds. The differences in the ultimate and elemental analysis of activated carbons produced from different raw materials under the same conditions indicate the dominant influences of the composition and structure of the precursors on their reactivity in the pyrolysis/activation reactions during steam pyrolysis.

The effect of the raw materials on the yield, physico-chemical characteristics and adsorption properties of the activated carbons obtained under the same conditions is shown in Tables 2 and 3. The samples obtained from apricot stones and almond shells have the largest BET surface area and total pore volume with significant prevalence of the micropores. The micropore volume and surface area of the

Table 3
Effect of the precursor on the porosity characteristics of the activated carbons

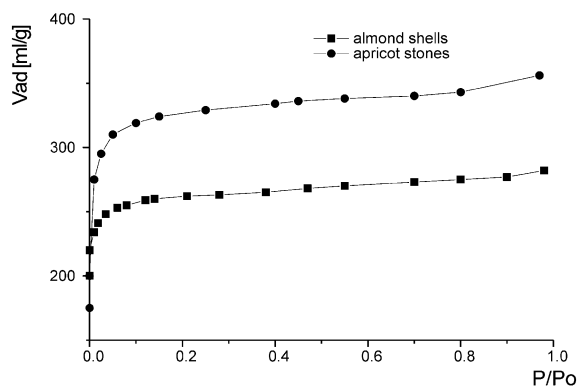| Raw material	Pore volume (cm^3/g)			
	Total	Micro	Meso	Macro
Apricot stones	0.83	0.50	0.11	0.32
Cherry stones	0.66	0.28	0.11	0.27
Grape seeds	0.58	0.12	0.18	0.28
Almond shells	0.82	0.40	0.06	0.36
Nut shells	0.67	0.21	0.13	0.33

Fig. 1. N_2 (77 K) adsorption isotherms of carbon adsorbents from agricultural by-products.

carbon obtained by steam pyrolysis of almond shells are comparable with those of activated carbons obtained by direct activation of almond shells with CO_2 to similar burn-off [20]. The comparison of adsorption capacities towards substances with different size of the molecules (N_2, iodine and methylene blue) shows that the carbon obtained from apricot stones is exclusively microporous. A part of its porosity is accessible to N_2 but not to iodine (i.e. microporosity less than 1 nm) and methylene blue (less than 1.5 nm). The other carbons are with microporosity accessible to iodine (i.e. microporosity greater than 1 nm).

The nitrogen adsorption isotherms of activated carbon obtained from apricot stones and almond shells are presented in Fig. 1. The adsorption isotherms obtained are of the IV type according to Brunauer et al. [21]. The share of the isotherms in the range of the relatively lower pressures (a step increase with a tendency for saturation) is typical for microporous adsorbents. The observed characteristics corroborate the presence of a considerable volume of micropores, where the adsorption proceeds on the principle of the condensation in pore volume and is in accordance with the high adsorption capacity of these samples. Table 3 shows that the carbon adsorbents obtained from cherry stones and grape seeds have predominantly macropores. The surface area of all carbons has alkaline character (Table 2).

The structural differences between the activated carbons produced under the same condition may be related to the differences in the chemical composition of the precursors. The lignin and holocellulose contents account for 95–97% of the agricultural by-products used in this study. The amount of cellulose is roughly 10% more in the almond shells and apricot stones than that in the cherry stones and grape seeds. We measured the porosity parameters of the chars produced by steam pyrolysis of samples of hydrolytic lignin and microcrystalline cellulose at 800°C for 1 h. It was determined that the macropores of lignin char constitute 70% of the total pore volume. The cellulose char, however, contains almost equal volumes of micro and macropores. Most likely, the behaviour of pure lignin and cellulose samples during steam pyrolysis experiments is different from that of lignin and cellulose combined in the structure of the parent materials. The porosity parameters of the chars obtained from different agricultural by-products suggest, however, that the differences in the lignin and cellulose contents of the precursors may influence the porous structure of the activated carbons. The relatively high microporosity of the carbons from apricot stones and almond shells can be partly attributed to the higher cellulose content of the raw materials. The data show that lignocellulusic material has a large effect on the pore structure of the activated carbons prepared by one-step pyrolysis/activation process at the same conditions. In contrast, some published results show that the pore structure of the carbon obtained by the two-step process is a function mainly of the activation experimental condition and does not depend much on the lignocellulosic material and the carbonization process used [22]. This difference may be explained considering that, in the case of N_2 carbonization, the structure of the obtained char does not depend much on the chemical composition of the precursors.

Table 4
Porosity characteristics of activated carbons[a]

Activ. carbon	N_2 BET surface area (m^2/g)	Pore volume (cm^3/g)			
		Total	Micro	Meso	Macro
A	1190	0.83	0.50	0.11	0.32
B	945	0.77	0.38	0.08	0.29

[a]Carbon A, activated carbon obtained by steam pyrolysis of apricot stones; Carbon B, activated carbon obtained after water vapour activation of the N_2 carbonized apricot stones.

Table 5
The material balances and pore volumes of activated carbons for both steam pyrolysis and pyrolysis in N_2 atmosphere of apricot stones

Treatment	Solid product (% yield)	Liquid product (% yield)	Gas + water + losses (% yield)	Pore volume (cm^3/g)			
				V_{total}	V_{micro}	V_{meso}	V_{macro}
Steam pyrolysis	41.5	18.7	39.8	0.83	0.50	0.11	0.32
Nitrogen pyrolysis	52.2	12.4	35.4	0.37	0.13	0.08	0.16

It is interesting to see the differences between the activated carbon obtained by steam pyrolysis of apricot stones (sample A) and carbon obtained by activation with water vapour of the apricot stones carbonized in N_2 (carbon B). The data (Table 4) show that when the percentage yield is comparable, carbon A has larger surface area and pore volumes than carbon B. The data obtained are in compliance with the experimental information described in the literature [20,23]. It was found that the activation is faster when carried out with the raw material than with the product carbonized in N_2. These differences may be explained considering that the material carbonized in N_2 has more ordered structure and less developed porosity than material carbonized in steam. This leads to a lower reaction rate of the material carbonized in N_2. These assumptions need a clearer explanation. The material balances and pore volumes for both steam pyrolysis and pyrolysis in N_2 atmosphere of apricot stones were determined to study the water vapour influence on the yield and properties of the products obtained. The data show (Table 5) that steam pyrolysis leads to a decrease in the solid yield and an increase in the liquid and gas yields compared to the product yields obtained after pyrolysis in a N_2 atmosphere. Higher yields of liquid and gas products by steam distillation contributes to the formation of a larger number of fissures and pores

and can be related to the formation of a well-developed porous structure of the solid products. On the other hand, water vapour is involved in chemical reactions in addition to steam distillation of the pyrolysis products from the surface of the sample. A larger surface area of steam carbonized material is accessible to the activation reagent molecules as the result of its more developed porosity. In summary the following basic comments can be made:

(a) Devolatilization of raw material during steam pyrolysis contributes to the formation of a large number of fissures and pores in the solid product. These pores and fissures may be blocked by the deposition of carbon from secondary reactions onto the solid surfaces. The presence of steam can prevent such deposition by removing primary volatiles from solid surfaces.

(b) In addition to the formation of more developed porosity and preventing secondary char formation on surfaces, steam can react with organic and inorganic matter for further activation of the carbon surfaces.

These factors increase the porosity and adsorptive capacity of the resulting carbons. The results are of practical significance since they mean that steam pyrolysis can be used to produce activated carbon with larger pore volume and surface area, instead of the

Table 6
Composition of gas obtained in steam pyrolysis of apricot stones

Component	vol%	wt%
Hydrogen (H_2)	22.4	1.8
Methane (CH_4)	18.1	11.2
Carbon monoxide (CO)	23.4	25.3
Carbon dioxide (CO_2)	35.5	60.7
Ethane (C_2H_6)	0.2	0.3
Propane (C_3H_8)	0.4	0.7
Caloricity (kJ/kg)		13,594.50

conventional two-step procedure. This will allow the decrease of heat expenses thus producing cheaper activated carbon of good quality.

3.2. Composition of gas obtained after steam pyrolysis of apricot stones

The composition of the gas evolved during steam pyrolysis of apricot stones is presented in Table 6. The data show that carbon dioxide, carbon monoxide and methane contents prevail in the gas. These gases may be formed as a result of destruction processes of biomass matter during steam pyrolysis. Parts of the carbon dioxide and carbon monoxide are also obtained by the interaction of water with solid residue in the process of treatment at the final temperature. The data also show that the gas as obtained can be used as energy sources.

3.3. Activated carbons from mixtures of furfural and tar from steam pyrolysis of apricot stones

The investigations on the composition of the tar from steam pyrolysis of apricot stones (TSPAS) show that the basic part of it is oxygen containing compound—derivatives of phenol, guaiacol, veratrol, syringol, free fatty acids and esters of fatty acids [24]. These structures can be involved in polycondensation processes. Thus, TSPAS can be used for the fabrication of monolithic carbon as a precursor for the production of activated carbons.

Earlier, it was determined that furfural resin is a suitable oxygen-containing raw material for the production of carbon adsorbents with a great number of oxygen-containing groups on the surface [25].

Furfural is an accessible and cheap material because there are many sources for its production.

Investigations for obtaining carbon adsorbents from mixtures of TSPAS and furfural are carried out in order to determine the possibility of the effective utilization of tar from steam pyrolysis of agricultural by-products. The adsorbents obtained from oxygen containing substances attract increasing attention because of the chemical character of their surface due to the oxygen-containing functional groups on it. Polymer precursors are especially preferred when carbon with low inorganic impurities is needed.

Carbon adsorbents with different structures and properties are obtained from mixtures of furfural and TSPAS varying the composition of the mixtures, activation reagents (water vapour and air) and conditions of treatment. Furfural accelerates the polymerization of the mixture and allows the reduction of the amount of H_2SO_4 added.

Table 7 shows that the oxidation treatment with air of a carbonized material produces an oxidized carbon with a predominantly macroporous structure. Due to this high reactivity, oxygen already reacts at the entrances of the pores and does not penetrate into the narrow pores.

The N_2 isotherms character (a step increase with tendency for saturation) is indicative of the microporosity of carbons activated with water vapour (Fig. 2). There are some differences in nitrogen isotherms of the three samples obtained from different mixtures. In the nitrogen isotherms of the activated carbon obtained from mixture containing 70% TSPAS the plateau begins at lower values of Vad. The nitrogen isotherms of the sample obtained from the mixture containing 70% furfural is steeper in the 0.3–0.8 range of relative pressures, thus indicating a larger development of mesoporosity in comparison with the samples obtained with larger content of TSPAS. The adsorption investigations reveal that the activation with water vapour leads to the formation of micropores as opposed to oxidation with air. This determines the considerably larger surface areas of carbons activated with water vapour compared to the carbons activated with air.

The data in Table 7 show that the differences in the furfural and tar contents in the mixture influence the pore texture and surface area of the carbon adsorbents obtained at the same conditions. The carbons obtained

Table 7
Porosity characteristics of activated carbons obtained from mixtures of biomass products[a]

Raw matter.	N_2 BET surface area (m^2/g)	Pore volume (cm^3/g)			
		Total	Micro	Meso	Macro
$S_{70:30}$	187	0.380	0.130	0.065	0.185
$S_{oxid.}$	441	0.485	0.125	0.082	0.278
$S_{activ.}$	1050	0.827	0.380	0.190	0.257
$S_{50:50}$	127	0.310	0.110	0.065	0.135
$S_{oxid.}$	291	0.395	0.115	0.078	0.202
$S_{activ.}$	795	0.575	0.265	0.112	0.198
$S_{30:70}$	110	0.275	0.102	0.060	0.113
$S_{oxid.}$	231	0.365	0.107	0.067	0.191
$S_{activ.}$	565	0.505	0.235	0.106	0.164

[a]$S_{70:30}$, carbon from mixture containing 70% furfural and 30% TSPAS. $S_{50:50}$, carbon from mixture containing 50% furfural and 50% TSPAS. $S_{30:70}$, carbon from mixture containing 30% furfural and 70% TSPAS.
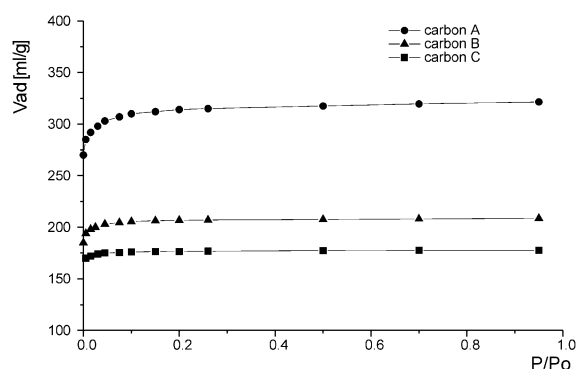

Fig. 2. N_2 (77 K) adsorption isotherms of carbon adsorbents from mixtures of biomass products: Carbon A, carbon adsorbent obtained from mixtures contained 70% furfural and 30% TSPAS; Carbon B, carbon adsorbent obtained mixtures contained 50% furfural and 50% TSPAS; Carbon C, carbon adsorbent obtained from mixtures contained 30% furfural and 70% TSPAS.

from mixtures with higher content of furfural possess larger surface area and more developed porosity. This fact may be explained considering that the carbon obtained from the mixture with a higher content of tar possesses a more stable to the gasification structure. In contrast the carbon obtained from the mixture with a higher content of furfural possesses a more disordered structure with faster reactions rate towards water vapour.

The proximate and ultimate analyses of the carbons oxidized and activated with water vapour (Table 8) indicate an insignificant ash content and a low sulphur content. The low sulphur content shows that sulphuric acid acts only as a catalyst of the polycondensation reactions. The oxidation with air at different temperatures leads to a considerable increase of the oxygen content in the oxidized carbon. The highest value is obtained when the oxidation treatment is performed at 400°C. The data also show that the increase of the furfural content in the mixture leads to the increase in the oxygen content of the carbon obtained.

The oxygen-containing functional groups on the surface are of great importance for the surface chemical properties of oxidized and activated carbons. The experimental data (Table 9) show that various oxygen-containing groups of acidic character and different chemical properties are present (carboxyl groups, carboxyl groups in lactone-like binding, phenolic hydroxyl and carbonyl groups). The formation of numerous oxygen structures during thermal oxidation treatment is also evident from the elemental composition of the starting and oxidized carbon, showing a considerable increase in the oxygen content (Table 6). The content of basic groups on the surface of carbon oxidized with air is considerably lower in comparison with the carbon activated with water vapour. The oxidation with air leads to a considerable increase of the amount of oxygen groups on the surface of

Table 8
Chemical composition of the carbon adsorbents obtained from mixtures of biomass products

Raw matter. and solid prod.	Proximate analysis (wt%)			Elemental analysis (wt%, maf)				
	W	Ash	pH	C	H	N	S	O
$S_{70:30}$	4.2	0.51	5.3	88.11	2.63	0.20	0.58	8.48
$S_{oxid.}$	4.8	0.81	3.9	66.28	2.12	0.23	0.32	31.05
$S_{activ.}$	5.8	0.71	8.1	80.17	2.47	0.21	0.19	16.96
$S_{50:50}$	3.9	0.69	6.7	88.59	2.74	0.31	0.62	7.74
$S_{oxid.}$	4.5	0.83	4.0	75.04	2.05	0.35	0.47	21.73
$S_{activ.}$	5.1	0.76	7.0	81.14	2.56	0.28	0.54	15.48
$S_{30:70}$	3.2	0.74	6.6	88.74	2.31	0.37	0.65	7.93
$S_{oxid.}$	4.6	0.88	4.7	81.73	2.02	0.39	0.41	15.54
$S_{activ.}$	5.2	0.81	7.0	84.87	2.21	0.37	0.31	12.24

Table 9
Acid-base neutralization capacities (m-equiv/g) of the obtained carbons

Sample	Base uptake (meq/g)				Acid uptake
	$NaHCO_3$	Na_2CO_3	NaOH	EtONa	HCl
$S_{70:30}$	0.110	0.272	0.600	1.760	0.545
$S_{oxid.}$	0.890	1.302	2.110	5.000	0.190
$S_{activ.}$	0.025	0.080	0.252	1.301	0.560
$S_{50:50}$	0.010	0.040	0.090	0.620	0.410
$S_{oxid.}$	0.580	0.690	1.300	2.220	0.260
$S_{activ.}$	0.016	0.023	0.029	0.847	0.575
$S_{30:70}$	0.070	0.142	0.240	1.310	0.460
$S_{oxid.}$	0.360	0.630	0.960	2.380	0.260
$S_{activ.}$	0.011	0.017	0.023	0.877	0.576

carbon. The enhancement of the content of carboxyl groups ($NaHCO_3$ consumption) is more significant. The increase of the content of phenolic (difference between NaOH and Na_2CO_3 consumption) and carbonyl groups (difference between NaOEt and NaOH consumption) is almost equal. The enhancement of the content of oxygen groups is more significant in the samples obtained from mixtures with higher content of furfural. This may be due to the larger surface area accessible for the oxidizing reagent. This leads to the formation of a larger amount of oxygen-containing functional groups. The oxidized carbon obtained from mixtures of TSPAS and furfural contains a larger amount of oxygen-containing functional groups than those oxidized at the same conditions, anthracite [26] and carbon from polyolefin wax [27]). This shows that the chemical composition of the precursors influences the chemical properties of the carbons obtained at the same conditions. The oxygen content of the precursors molecule considerably increases the content of oxygen structures in the final product.

The sample activated with water vapour contains predominantly oxygen-containing groups with basic character (Table 9). These data are confirmed by the results of the pH measurements. It can be seen (Table 8) that the pH of the sample oxidized with air is 3.9 while that of the sample activated with water vapour is 8.1.

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                    ┌─────────────────┐
                    │     BIOMASS     │
                    └─────────────────┘
              ┌──────────┼──────────────┐
              ↓     Steam │ Pyrolysis    ↓
    ┌──────────────────┐ ┌─────────────────┐ ┌─────────────────┐
    │ CARBON ADSORBENTS│ │ LIQUID PRODUCTS │ │  GAS PRODUCTS   │
    │with alkaline     │ │                 │ │                 │
    │character         │ └─────────────────┘ └─────────────────┘
    │of the surface    │          │
    └──────────────────┘          ↓
                    ┌─────────────────────┐
                    │ Mixtures with furfural│
                    │  and  H₂SO₄          │
                    └─────────────────────┘
                              │
                    Polycondenzation
                     carbonization
                              ↓
                    ┌─────────────────────┐
                    │   SOLID PRODUCT     │
                    └─────────────────────┘
                              │
                    activation │ oxidation
                              ↓
                    ┌─────────────────────┐
                    │ CARBON ADSORBENTS   │
                    │with alkaline and acidic│
                    │character of the surface│
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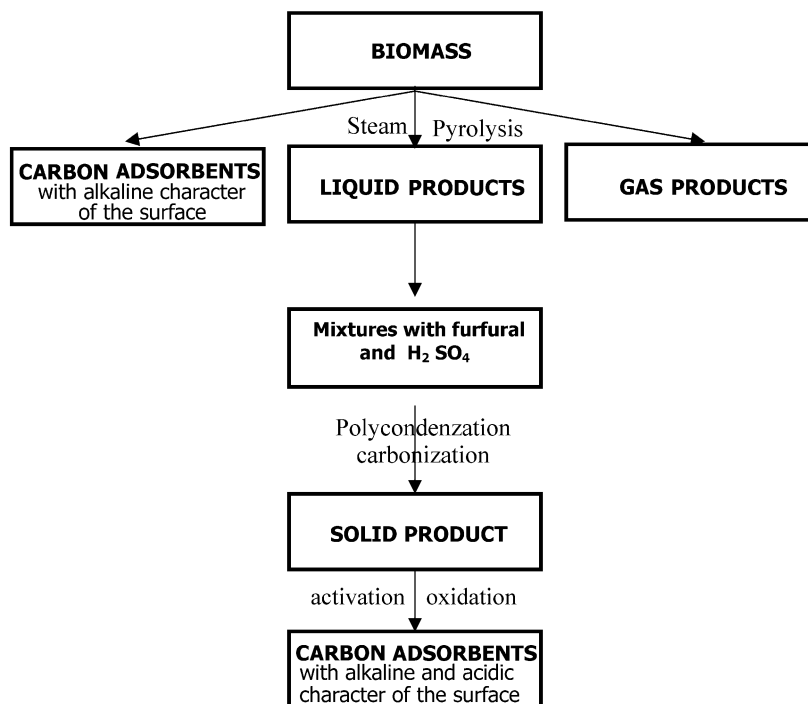
Fig. 3. Production of carbon adsorbents and gas products from biomass.

These preliminary investigations show that the chemical composition of the polymer precursor influences the porosity, surface chemistry and adsorption characteristics of the carbons obtained at the same conditions. For producing the activated carbons with similar physico-chemical characteristics the activation conditions of the solid products obtained from different mixtures should be optimized.

4. Conclusions

The results described in this work show that steam pyrolysis produced different types of activated carbon from different agricultural by-products. The final physico-chemical properties of the activated carbons obtained at common conditions depend on the composition and the plant texture of the corresponding raw materials. Materials with a greater content of lignin (grape seeds, cherry stones) develop activated carbons with macroporous structure, while raw materials with a higher content of cellulose (apricot stones, almond shells) yield activated carbon with a predominantly microporous structure. Steam pyrolysis of raw material produces a larger development of porosity than activation with water vapour of material carbonized in N_2.

Mixtures of furfural and tar from steam pyrolysis of apricot are appropriate raw materials for obtaining carbon adsorbents with insignificant ash and sulphur contents. Pore volume, pore size distribution and chemical character of surface of carbon adsorbent obtained depend on the composition of the mixture, activation reagent and temperature of treatment. The activation is faster when carried out with carbon obtained from the mixture with higher content of furfural. A great number of oxygen-containing groups are established on their surface. The nature of functional groups reveals that carbon adsorbents obtained from mixtures of furfural and tar from steam pyrolysis of apricot stones are polyfunctional cationites.

The results of our investigations allow the creation of a process for effective utilization of biomass (Fig. 3). This process included: 1. Obtaining carbon

adsorbents with alkaline character of the surface, liquid products and energy gas by steam pyrolysis of biomass. 2. Obtaining carbon adsorbents with acidic and alkaline character of the surface from biomass tar and mixtures of tar and furfural. This process gives the possibility of the effective utilization of biomass.

References

[1] Larson ED. Advanced technologies for biomass conversion to energy, Proceedings of the Second Olle Lindstrom Symposium on Renewable Energy-Bioenergy, Royal Institute of Technology, Stochholm, Sweden, 1999. p. 1–13.

[2] Gonzalez MT, Rodriguez-Reinoso F, Garcia AN, Marcilla A. CO_2 activation of Carbonized under different experimental conditions. Carbon 1997;35:159–62.

[3] Gonzalez JC, Sepuveda-Escribano A, Molina-Sabio M, Rodriguez-Reinoso F. Preparation of activated carbons by chemical activation of olive stones. The European Carbon Conference "Carbon 96"-Newcastle, UK, July 1996. p. 519.

[4] Rodriguez-Reinoso F, Molina-Sabio M, Gonzales MT. The use of steam and CO_2 as activating agents in the preparation of activated carbons. Carbon 1995;33:15–23.

[5] Toles CA, Marshall WE, Johns MM. Granular activated carbons from nutshells for the uptake of metals and organic compounds. Carbon 1997;35:1407–14.

[6] Molina-Sabio M, Caturla F, Rodriguez-Reinoso F. Influence of atmosphere used in the carbonization of phosphoric acid impregnated peach stones. Carbon 1995;33:1180–2.

[7] Gonzalez JC, Gonzalez MT, Molina-Sabio M, Rodriguez-Reinoso F, Sepulveda-Escribano A. Porosity of activated carbons prepared from different lignocellulosic materials. Carbon 1995;33:1175–7.

[8] Toles CA, Marshall WE, Johns MM. Surface functional groups on acid activated nutshell carbons. Carbon 1999;37:1207–14.

[9] Rivera-Utrila J, Ferro-Garcia MA, Mata-Arjona A, Gonzalez-Gomez C. Studies on the adsorption of ceasium, thallium, strontium and cobalt radionuclides on activated carbons from aqueous solutions. Journal of Chemical Technology and Biotechnology 1984;34A:243–8.

[10] Ferro-Garcia MA, Rivera-Utrila J, Rodriguez-Gordillo J, Bautista-Toledo I. Adsorption of zinc, cadmium, and copper on activated carbons obtained from agricultural by-products. Carbon 1988;26(3):363–73.

[11] Morawski AW, Sobocinska D, Kalenczuk RJ, Katucki K. Application of modified synthetic carbon for adsorption of trihalomethanes (THMs) from water. The European Carbon Conference "Carbon-96"-Newcastle, UK, 1996. p. 254.

[12] Minkova V, Razvigorova M, Goranova M, Ljutzkanov L, Angelova G. Effect of water vapour on the pyrolysis of solid fuels. Fuel 1991;70:713–9.

[13] Gergova K, Galushko A, Petrov N, Minkova V. Investigation of the porous structure of activated carbons prepared by pyrolysis of agricultural by-products in a steam of water vapour. Carbon 1992;30:721–7.

[14] Brunauer S, Emmett P, Teller E. Journal of the American Chemical Society 1938;60:309.

[15] Barret EP, Joyner LC, Halenda PH. Journal of the American Chemical Society 1951;73:373.

[16] Defay R, Priyogine J, Bellemans A, Everett DH. Surface tension and adsorption. London: Longman, 1966. p. 218.

[17] Gregg SJ, Siny KSW. Adsorption surface area and porosity. London: Academic Press, 1982. p. 218.

[18] Boehm HP. In: Eley DD, Pines H, Weisz PB, editors. Advances in catalysis, vol. 16. New York: Academic Press, 1966. p. 179.

[19] Papirer E, Li S, Donnet J-B. Carbon 1987;25(2):243.

[20] Linares-Solano A, Lopez-Gonzalez D, Molina-Sabio M, Rodriguez-Reinoso F. Active carbons from almond shells as adsorbents in gas and liquid phases. Journal of Chemical Technology and Biotechnology 1980;30:65–72.

[21] Brunauer S, Deming LC, Deming WE, Teller E. Journal of the American Chemical Society 1940;62:1723.

[22] Gonzalez JC, Gonzalez MT, Molina-Sabio M, Rodriguez-Reinoso F. Carbon 1995;35:1175.

[23] Rodriguez-Reinoso F, Martin-Martinez JM, Molina-Sabio M, Perez-Lledo I, Prado-Burguete C. A comparison of the porous texture of two CO_2 activated botanic materials. Carbon 1985;23:19–24.

[24] Razvigorova M, Goranova M, Minkova V, Cerny J. On the composition of volatiles evolved during the production of carbon adsorbents from vegetable wastes. Fuel 1994;73:1718–22.

[25] Petrov N, Budinova T, Razvigorova M, Ekinci E, Yardim F, Minkova V. Preparation and characterization of carbon adsorbents from furfural. Carbon 2000;38:2069–75.

[26] Budinova T, Petrov N, Minkova V, Razvigorova M. Influence of thermooxidative treatment on the surface properties of anthracite. Fuel 1998;77(6):577–80.

[27] Petrov N, Budinova T. Oxidized Carbon from Polyolefin Wax. Chemie-Ingenieur-Technik 1992;64(1):64–6.