Turning wastes into high grade ecoproducts

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Abstract: - The nature of precursors has a strong influence on the structure and properties of the activated carbons (AC). At the same time, their adsorption capacity is determined by the condition of manufacturing during the thermal processes. This study was undertaken to provide some new data on the ecoproducts manufacturing starting from vegetal wastes re-use. A summary of the experimental conditions used in this work by pyrogenation/carbonisation at 550-650^{0}C, followed by physical activation process at 950 – 1000 ^{0}C, are included. The new ecoproducts proven a uniform porous structure developed mainly of micropore giving good adsorptive properties.

Key-Words: - wastes re-use, renewable ecoproducts, adsorption, microporosity, depollution

1 Introduction

Despite remarkable progress made in the recent years in all industries concerning ecological efficiency, a great effort remains to be done until sustainable standards will be reached. There is a visible orientation world-wide focused on the using of renewable ecoproducts, whose obtaining is less expensive and doesn't involve waste purification processes.

In the last decades, AC has been proven as being very efficient in a wide number of applications for the removal of air and water pollutants [1-3].

There is a large variety of raw materials from which AC can be obtained: wood, coconut shells and fruit pits (olive, peach), peat, brown coal, lignite, bituminous coal, petroleum coke, agricultural byproducts (palm kernel shells, rice straw), other vegetable wastes, sawdust.

Wood, the classical raw material is very expensive and defficitary, 1 to of AC results from 500 m^2 forests, which could consume ~ 0.7 to/year CO_2 and produce ~ 0.75 to/year O_2.

The widening of the raw materials basis for producing AC towards other vegetal waste could significantly contribute to a more sustainable utilization of the natural resources, being in accordance to the EU policies. On the other hand, vegetal wastes have a negative impact on the environment due to the extended surface of the disposal area, possible pollution of surface and ground waters and mostly due to the rising of the CO_2 emissions resulted by actual incineration. For example, even the most used waste as biomass, sawdust is deposited in the villages on simple field areas or along the rivers sides.

In Romania, the statistics reveal that the quantities of industrial and agricultural wastes present a positive trend and mostly, the wastes are eliminated by storage. Every year, in Romania are reused between 15-20% of industrial wastes. The industrial wastes are stored in the producers own deposits – dedicated or ad hoc organized. Actually, chip/particleboard producers are confronted with a serious problem on waste disposal and transport, the only solution being represented by landfill. Additionally, thousands tones of hard and soft agricultural materials are produced in Romanian plain, the majority of which is left in the fields as agricultural waste. The consumption of ecoproducts, as are AC, on the domestic market, used either for cleaning purposes, and during technological processes for water purification, is assessed for the year 2012 at the minimum level of 6,500-10,000 tones. The estimated demand for short term with an estimated annual growth of 2-3% based on the necessity of the implementation of the EU *Acquis* in the field of environment protection, would have a considerable effect on the people's health and quality of life.

Our aim in this paper is to describe the possible transformation of some industrial and agricultural wastes of vegetal origin into AC, as a cost benefit opportunity to develop ecoproducts, beside the environmental aspect of proposed friendly technologies. In addition, one of the proposed waste streams represents a technical novelty: the recycling of coated chip/particleboard wastes. Other vegetal wastes proposed to be used are those resulted from the wood and natural fibers (textile) processing industry, and agricultural wastes that are not used in other purposes. The clean technology uses exhaust gas resulted from the combustion of released volatile matter as energy supplement and supplier of physical activation agents, and the recovery of the energy excess as hot water and preheated air for the combustion chamber.

2 Experimental

The wastes were provided by:

- *Industry* (wood, textile, pulp and paper, plants processing), as: particleboard wastes *(chipboard, Medium Density Fiberboard-MDF, and Oriented Strand Board-OSB, including high toxic- HT- resins)*, furniture screws (sawdust, chips, board and veneer wastes); textile (processed and no-processed natural fibers); paper wastes and waste plant extraction products (sorghum bagasse and medicinal plants);
- *Agriculture*, hard lignocelluloses wastes (fruit kernels of peach, apricot, plums, olives, nut shells) and soft lignocelluloses wastes (cereals straw, corn), technical plants (sunflower stalks, soybean hulls), medicinal. On categories the wastes ash content is presented in Table 1.

Table 1. The wastes ash content

Wastes type		Ash, db,%
Industrial	Agricultural	
Wood (unprocessed)	Fruit kernels	0.5-1.2
Textile (cotton)	Fruit shells	0.6-1.8
Wood (processed PAL *-including HT resins*)	Cereals, technical plants	1.0-2.5
Plants processing (Sorghum bagasse, sunflower stalks)	Medicinal plants	3.0-4.0
Pulp und paper	Leguminous plants	4.0-9.0
	Other technical plants	Over 9.0

(db=anhydrous)

2.1 Raw material preparation

To increase the specific weight and thus, the yield of the resulted char, the wastes have been briquetted with and without binder, by pressing into a cylindrical mould at different pressures, Fig.1.

As compared to classical briquetting theory we could appreciate that wastes agglomeration is theoretical substantiate by:

- Physical and physical-chemical phenomena which take place during pressing (molecular attraction, capillary forces);
- Plants chemical components behavior during pressing cellulose, lignin, hemicelluloses, resins, tannin, etc.

Sampling, preparation and wastes analyzing followed the national standard laboratory methodology, according to ISO. Laboratory results show the most appropriate AC quality for the wastes having low mineral matter (A^{db}: 2-5%), high carbon (C^{daf}: 85-95%) and the original botanical cell texture that determines the developed chars microporosity. The disadvantage of low AC yields is balanced by the low cost of the feedstock and other ecologically advantages (i.e. possibility of heavy metals and polar-organic compounds removing) [4].

a b

Fig.1 Different types of waste raw briquettes (sawdust, cotton, paper, cereals) and soybean hulls char.

2.2 Char and AC preparation and characterization

The following main operation was required by the laboratory scale experiments: low-temperature carbonization (I) and char physical activation (II), Fig.2.

In our work, the technical solution of char manufacturing consists on wastes direct heating in a rotary kiln. at 550-650^{0}C by direct contact with hot gases (700-800^{0}C) resulted from incomplete burning, with a heating rate of 8-9^{0}C/min, for a reaction time of maximum 60 min. The necessary heat amount, which provides the physical and chemical transformation of the wastes, is represented by the thermal heat of the exhausted gases produced in the combustion chamber. The char conversion process takes place in reducing medium, with a max. 0.3 O_2 [5-8]. The clean technology adopted uses burned gases resulting from the combustion of exhausted volatile matter (tar vapours, pyrogenetic water vapours, aromatic hydrocarbons, acetone, methanol, acetic acid, fuel gas, etc.) as energy supplement and physical activation agents providing for processes of conversion into charcoal and activation, and the excess to heat up water and preheat air for the combustion chamber. The equipment is simplified, excluding the cooling, condensing, separation and purification operations of water [9-11]. The properties of the char were determined by the type of raw materials as well as by the pyrogenation process, temperature and retention time in the oven [12-14].

The activation was performed at 950-1000^{0}C with a high enthalpy of the burned gases input ~ 400 kcal/m^{3}N. The process took place in a vertical kiln, which was selected having in view the decrease of the activation time by intensifying the mass and heat exchange with the inlet of exhaust gases at min.1200^{0}C and a composition of CO_2 (13-13.5%), H_2O (20-22%), N_2 (64-67%) [15].

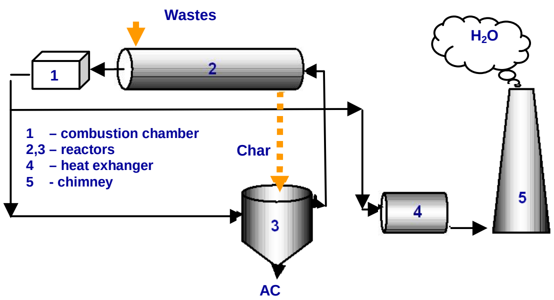


Fig. 2 Schematic flow sheet of the clean technology.

The activating agent is the mixed superheated steam and CO_2. After activation which is an endothermic process, gases containing CO and H_2, are burned into the combustion chamber. The excess of heat gas is used to heat up water and preheat air for the combustion chamber [12,16,17].

The properties of the intermediate and final product were determined by measuring the ash and carbon content, bulk density, the iodine number and the specific surface area BET. The products, both char and AC, were characterized in order to reveal their developed pore network and adsorption capacity suitable for the intended application [18]. The porosity and pore distributions of selected samples were determined for pores in the range 5-300Å radius. Before porosimetrical studies, the samples were dried for 3 hrs at 105 ^{0}C and degassed to a residual pressure of 10^{-2} torr, at 300^{0}C for 1 hr. The surface area BET and the total pore volume have determined by N_2 adsorption isotherms at 77.8^{0}K.

3 Results and discussion

A substance which contains both cellulose and lignin is lignocelluloses. Lignocelluloses materials include besides wood, any agricultural wastes. Generally, what is valid for wood is valid for any kind of lignocelluloses materials, even some differences in chemical composition and morphology occurs. The walls of the vegetal cells are made of cellulose which sometimes is found in the form of fibers. It is intimately mixed with variable quantities of lignin, hemicelluloses, fats, resins and inorganic substances, Fig 3, [19].

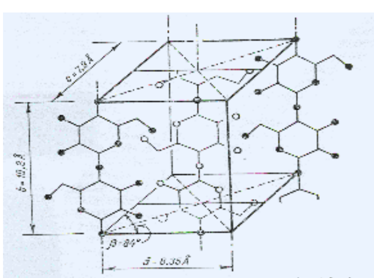


Fig. 3 Spatial representation of cellulose elemental unit

The analytical results from Table 1 reveal that both industrial and agricultural wastes chosen are suitable for the processing steps of carbonization and activation.

The low inorganic content is a key parameter because the ash components play an important role in the adsorption process. They can modify the interaction between the AC surface and the molecules to be adsorbed. An important aspect of the ash chemistry is the catalytic effect in case of physical activation. This determines the selective formation of the pores being preferential of large sizes close to the catalytic particles; these results in the diminishing of the AC adsorption capacity.

For the industrial wastes, especially provided by textile and wood sectors, we noticed the high purity of the raw material, of maximum 2.5% ash content (db). For the agricultural wastes the inorganic content is less accumulated in hard lignocelluloses wastes (kernels, shells) in which the mean value is of 1%. The results confirm that the volatiles content, representing more than 70% (db) of the raw material, does not depend on the type and source of the investigated wastes. Thus, it could offer the premise of a decrease in fuel consumption in the char manufacture stage.

The development of porosity during wastes carbonization is mostly influenced by the manner in which the thermal treatment is carried out: fast or slow and on direct or indirect heating conditions. In our case, the technical solution chosen of direct heating, offers the intimate contact between the hot gases and wastes that involve through the endothermic reactions, the direct transfer of the heat to the solid material. The main advantage is the development of a better porous network in the resulted char.

The formation of the char wastes can be compared to that of wood, taking into account their both vegetal origins.

The primary chemical reactions which taken place is presented in equations (1), (2) [20].

$2C_{42}H_{60}O_{28} \rightarrow 3C_{10}H_5O + 19\ H_2O + 3CO_2 +$
wood primary char moisture carbon dioxide
(100 %) (28.8 %) (16.8 %) (6.5 %)

$+ 2.5\ CH_3COOH + HCOOH + HC_3OH + C_{36}H_{43}O_{16} +$
primary tar
(7.5%) (2.2 %) (1.6 %) (36.0 %)

$+ C_5H_8O$
oils from primary tar (1)
(4.2 %)

In the second stage, the primary tar decomposes:

$C_{36}H_{43}O_{16} \rightarrow C_{30}H_{22}O_3 + H_2O + CO_2 +$ hydrocarbons
primary tar secondary char
(36.0 %) (21.1 %) (8 %) (4.3 %) (2.8 %) (2)

At 550 – 650 °C the edges of C – C cross-linked structures start to lose their stability because of polymerization. One part remains unsaturated and others react with H_2, becoming saturated. The first are volatilized as tar vapors and the last are condensing as char with a high content of aromatic hydrocarbons.

The data show that the obtained wastes char have improved characteristics, even than of wood, Table 2 [4,21].

Table 2. Characteristics of the char wastes

Wastes Char	Physical-chemical characteristics*)			
	Ash A^{db}, %	Volatile V^{db}, %	Fixed carbon C_{fix}, %	Iodine value, mg/g
Wood				
unprocessed	Max.5	Max.12	Min.85	Min.500
processed (particle-board *including HT resins*)	Max.8	Max.11	Min.80	Min.200
Cotton	Max.5	Max.13	Min.80	min.500
Paper	Max.5	Max.8	Min.85	Min.500
Hard agricultural				
kernels	Max.5	Max.8	Min.85	Min.250
shells	Max.3	Max.11	Min.85	Min.250
Soft agricultural				
cereals	Max.15	Max.18	Min.65	Min.200
technical plants	Max.12	Max.10	Min.75	Min.200
leguminous	Max.18	Max.18	Min.60	Min.200
medicinal	Max.25	Max.20	Min.50	Min.200

To obtain AC from vegetal wastes, the raw material that first was pyrolysed is than partially oxidized with steam CO2 at higher temperatures. Carbonization temperature has important effects in changing the structure of the porous material subjected to activation. An AC with a wide surface area and a higher adsorptive property is made only by special char gasific ation process.

It is necessary a high temperature (over 1200°C at the outlet of the exhausted gases from the combustion chamber) to increase the rate of endothermic reactions between raw material and activation agents. Some reactions are possible [3, 9, and 12]:

$C + H_2O \rightarrow CO + H_2$ $\Delta H = +117$ kJ/mol (3)

$C + 2H_2O \rightarrow CO_2 + 2H_2$ $\Delta H = +75$ kJ/mol (4)

$C + CO_2 \rightarrow 2CO$ $\Delta H = +159$ kJ/mol (5)

The energy balance is improved by burning the reaction products into the combustion chamber, which generates the mixt steam and CO_2 activation agents:

$CO + ½ O_2 \rightarrow CO_2$ $\Delta H = -285$ Kj/mol (6)

$H2 + ½ O_2 \rightarrow H_2O$ $\Delta H = -238$ Kj/mol (7)

The results are presented in Fig. 4.

The surface area BET increase as the type of waste has a more pure structure. The surface area BET passes through a maximum (919 m^2/g in case of wood wastes and 826 m^2/g in case of cotton wastes) after that slightly decreases (696-814 m^2/g in case of fruit kernels), being correlated with the results of some commercial samples of wooden origin, which reaches surface area between 733-914 m^2/g. The results obtained in case of soft lignocelluloses materials are very promising, showing the influence of the raw material quality on the adsorption capacity of the AC.

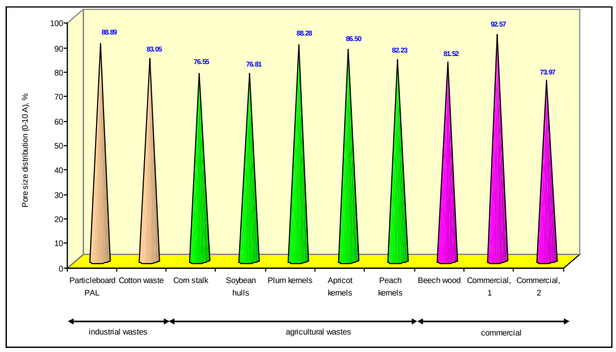


Fig.4 Surface area BET in case of AC of different wastes

The values are mainly over 80% for the AC obtained from hard lignocelluloses materials and over 75% for those obtained of soft agricultural wastes, Fig. 5.

The average radius of pores emphasizes the similarity between the samples of AC made of wastes, with radius between 6.9-9.7 Å and those obtained of wood (7.95 Å) or the commercial activated carbons of 6.69 - 8.0 Å. The size of pores radius has a particular influence on the diffusion rate of adsorbent molecules on the adsorbent surface, as well as on the selectivity, versus the different types of molecules in gaseous and liquid environments, which follow to be cleaned.

The percent distribution of pores on sizes certainly emphasizes the existence in the AC samples obtained experimentally of a porous structure formed especially from ultra-micropores 0-10 Å.

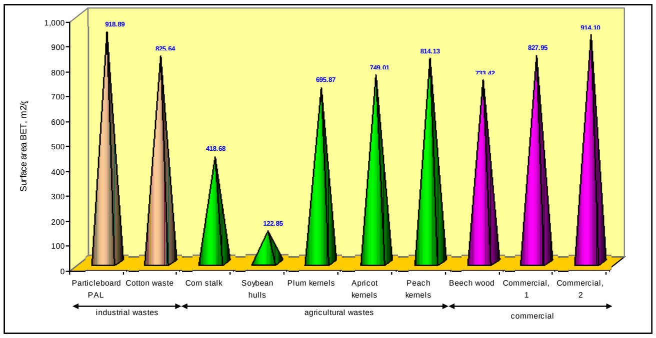
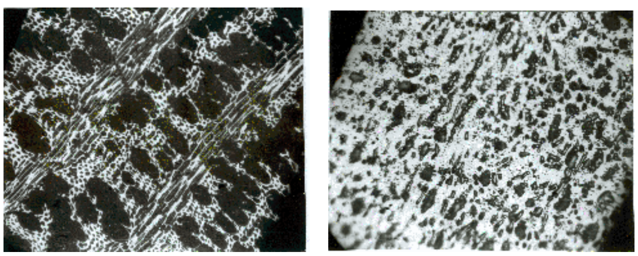


Fig.5 Pore size distribution between 0 – 10 Å in AC of different origin.

The encouraging results obtained on the AC porosity type and range, highlight the compatibility between different types of raw materials based on the structure of the same vegetal origin. The microstructural studies on the activated carbon reveal the aspect of textures in steam-CO_2 gasification processes, Fig. 6, [22].



a b

Fig.6 Photomicrographs of some activated carbons of vegetal origin, under reflected light, oil immersion, 375X: (a) Very fine porosity, with round pores bounded by radial chains with elongated pores in wood activated carbon. (b) Fine porosity developed in fruit-kernels activated carbon with thin pore walls and very fine porosity.

To establish the AC characteristics on waters depollution, we have started preliminary tests during static conditions, on different organic substances as: phenol, benzene, toluene and xylene (BTX), [23]. The removal of volatile organic compounds (VOC) from gases allowed the possibility as technical novelty to anticipate over 90% of VOC removal from the air streams (ethyl acetate, toluene, methylene chloride) and possibly, heavy metal contaminants from polluted waters.

The results obtained during gas chromatograph experiments will be the subject of another paper.

4 Conclusion

In Romania, the vegetal origin wastes provided by some industrial and agricultural fields, due to their physical-chemical and structural characteristics, could become promising materials for the production of carbon base sorbents, char and AC, for waste waters preliminary purification.

Because the AC are successfully applied for the waste waters purification, it is necessary to find new materials that are similar to classical adsorbents - based mainly on wood and coals - on long term available and profitable.

The porous structure of AC depends strongly on raw material characteristics and processing parameters during carbonization and activation. According to their adsorption characteristics the results show satisfactory specific surface areas, depending on the type of raw material, of hard or soft consistency.

The adsorptive properties increase as the inorganic matter of the parent raw material decrease.

The pore size distribution reveals a satisfactory repartition of pore volume in the domain of ultramicropores (0-10Å) of over 70-80% for the activated char samples.

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