ACTIVATED CARBON FROM OIL PALM SHELL OBTAINED BY SUPERCRITICAL WATER TREATMENT

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Introduction

Activated carbon is one of the most important types of industrial carbon with very high porosity and surface area. It is prepared by carbonization and activation of a large number of raw materials of biological origin such as coconut shells, wood, peat, coal and fruit stones [1, 2]. In general, the raw materials to make activated carbon must accomplish a sort of requirements like high carbon content, low mineral content, easily activation, low degradation during storage, and, of course, low cost [2]. Agro-industrial by-products such as coconut shells, almond shells, hazelnut shells, cherry stones, eucalyptus, apricot stones, nuts, grape seeds, olive and peach stones, sugar cane bagasse and oil palm trunks are materials usually inexpensive and abundantly available for which the effective utilization has been desired [3-5]. Therefore the preparing of activated carbon with high surface area from an agricultural by-product would be an interesting subject [5].

Oil palm shells from palm oil processing mills is an agricultural solid waste in some tropical countries [3]. Colombia is the fifth Oil Palm *(Elaeis guineensis)* producer in the world, with almost 450.000 tons per year. The Oil Palm plants in this country produce 140.000 tons of Oil Palm Shell, a waste used in boilers or in roads improvement. Besides, the government plans includes the Palm crops in the program for illegal crops substitution, which means the plantations will raise in production and byproducts. The conversion of these cheap and abundant waste into activated carbon has been studied for several authors using different methods of activation [3-5]. Supercritical water has been used as extraction method and only as activation agent by Sánchez et al [6]. The aim of this work was obtain activated carbon by supercritical water treatment after carbonization of oil palm shells.

Experimental

The Oil Palm Shells where washed with distilled water and left to dry several days on ambient temperature (approximately 291 K). These where later classified with a CIV of DIN 4188. The samples selected where the ones retained on the 4 and 6,3 mm CIV. A BET superficial area analysis was done on all samples using a Micromeritics Gemini III 2375K at 77K and a Micromeritics VacPrep 061 degasification unit. In order to establish the decomposition characteristics of Oil Palm Shells, TGA analysis was performed using a 60 cm^3/min nitrogen flow with a heating rate of 1,5 K/min until 1723 K where reached.

The carbonization process was done using a Stanton Redcroft oven, with heating capacity up to 1273 K, under a nitrogen rich atmosphere inside a quartz reactor with measured 1,5 inches in diameter and 20 inches in length. The temperature inside the reactor was controlled using a Watlow Series 96 controller and a Type j Termopar (Fe-Co).

Supercritical water was used for activation of Oil Palm shells chars. This was done in an stainless steel reactor (Autoclave Engineers) for high pressures, with capacity of 300 cm^3, maximum operation temperature of 727 K and maximum operation pressure of 5.200 psi. The setup also used an Autoclave Engineers relief valve for 20.000 psi, an Ashcroft manometer with measuring range from 0 to 10.000 psig, an Autoclave Engineers heating blanket, a Watlow Series 96 controller and a Type j Termopar (Fe-Co).

Carbonization and activation process were developed under conditions listed in table 1. The activation process was always done feeding the reactor with the shell chars besides 170 cm^3 of distilled water, all in a batch process. It was used a 10 K/min heating rate. Once reached the operating pressure and the temperature that guaranteed the supercritical state, the process was left running for 60 and 120 minutes. Upon conclusion of activation time, heating was suspended and the reactor was brought to a pressure of 1500 psi opening the relief valve to evacuate volatile components and water vapor, until activated carbon was completely dry. This was done to facilitate subsequent analysis of iodine number, ashes, humidity, superficial area and SEM.

For adsorption capacity testing, a CO_2 test was done using a Parr® calorimetric pump. Measures were done using a Haenni® membrane manometer and a pressure 0.1 psi precision controller. The pump was fed with the material and closed. Air was removed from inside. Pressurized CO_2 was introduced and the descent of pressure was measured until the system was stabilized. To ensure that pressure changes occurred only by adsorption meanings and not by leaks in the pump, hermetic stability was measured at all times.

Table 1. Carbonization and activation processes conditions

Sample	Carbonization			Activation		
	Temperature, K	Time, min	Burn-off, %	Pressure, psi	Time, min	Efficiency. %
SCW1	723	60	71.2	3500	60	86.62
SCW2	723	60	71.2	3500	120	85.01
SCW3	723	60	71.2	4800	60	82.43
SCW4	723	60	71.2	4800	120	81.20

Results and discussion

The characteristics of the starting material and the activated carbons are listed in table 2.

Table 2. Proximate analysis of oil palm shell and activated carbons

Sample	Original Oil palm Shell					
	Humidity, %wt	Volatile matter, %wt	Fixed carbon, %wt	Ashes, wt%	Surface area BET, m^2/g	Iodine Number
Oil Palm Shell	7.42	67.42	29.97	2.61	18	
	Activated Carbons from Oil Palm Shell					
SCW1	7.61			5.28	539	448
SCW2	5.82			4.24	562	456
SCW3	5.42			5.04	599	488
SCW4	4.18			5.02	671	526

Oil Palm shell is a high matter content material, and low ashes content. Because of its hardness, it's optimal for get a granular product. It is a good raw material for preparation and production of activated carbon, with a high density and low surface area. Figure 1 shows weight losses in shell decomposition, during TGA. Material loss non-linked humidity fast, until 403 K. At this point, weight is constant until 498 K. From here, there is a vertiginous weight loss because of decomposition of cellulose, hemicelullose and lignin. Two firsts decompose in a relative narrow range, between 498 K y 648 K. Lignin is the component which starts the decomposition first, at a lower temperature (383 K). However, its pyrolysis happens in a very large temperature range, almost 900 degrees, with low decomposition rates. The residue presents at last a considerable fraction of the original matter [7].

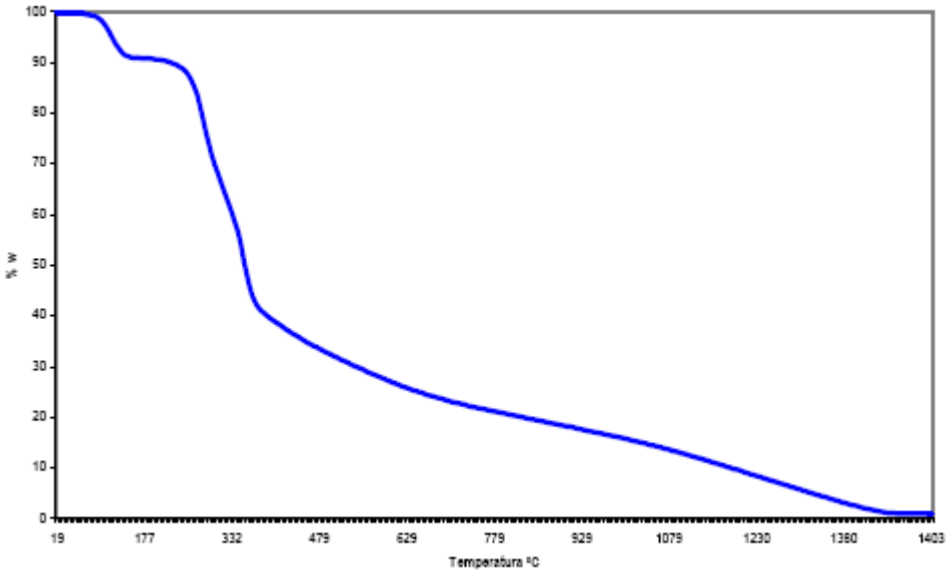

Figure 1. Oil Palm Shell TGA.

Ashes values showed in table 2 for activated carbons are lower than reported in other works with the same material, but different activant agent, like CO_2. This could be explained for SCW dissolving power, for organics and inorganics materials. The difference, for similar activation conditions, is close to 1,07%. Humidity values were low for strongest conditions in the process (activation – carbonization), and it was observed a sensible decrease comparing this values with the values of initial shell.

Surface area values for activated carbons are different in 20% with iodine numbers. BET area values were acceptable, but lower than commercial activated carbons. Table 2 shows values between 539 and 671 m^2/g, which are low but so bigger than 18 m^2/g of Oil Palm shell without any treatment. Better surface area was founded for sample SCW4, with 4800 psi by 2 hours, while lower was the sample SCW1, activated to 3500 psi by 1 hour. SCW2 sample, 3500 psi by 2 hours, reach 562 m^2/g, and SCW3, 4800 psi by 1 hour, reach 599 m^2/g.

This could be an indication of the direct relationship between surface area and pressure, as much as activation time. However, there is a limit. When it was tested hardest activation conditions, 4800 psi by 3 hours, it was obtained an area of 197 m^2/g, lower than SCW4 sample area, activated with the same pressure but different time. SEM images show the presence of pores in the surface, and the fissures in the material as a process consequence at the work conditions. The activated carbon adsorption capacity for gases in similar conditions of industry

could be appreciated with CO_2 adsorption test. The reached value for CO2 adsorption was 22,4 mmol/g carbon.

If the BET surface area value are compared with earlier works done with different activation conditions, but the same material, it could be notice similar results with similar carbonization conditions [3].

Conclusions

Oil Palm shell is a good raw material for preparation and production of activated carbon. Supercritical water treatment is a good new method for activation which develop acceptable surface areas. Best activation conditions were 4500 psi by 2 hours, producing activated carbons with areas until 671 m^2/g.

Acknowledgments

The authors are very thankful with people of Laboratorio de Investigación en Combustibles, Departamento de Química, Universidad Nacional de Colombia.

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