



Activated Carbon from Sugarcane Bagasse Prepared by Activation with CO₂ and Bio Oil Recuperation

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The aim of this work was to prepare activated carbon (AC) from sugarcane bagasse by the physical activation process (CO₂) and subsequently evaluate the physicochemical characteristics of the AC and of the bio oil produced. In a physical activation process, the biomass is pyrolysed, under an inert atmosphere (N₂), and the resulting char with small adsorption capacity is subjected to a partial and controlled gasification at high temperature with carbon dioxide to afford adsorbents with high specific areas. Furthermore, in the pyrolysis step there is the production of bio oil, which is a liquid with a high energy density and it is able to substitute conventional fuels in different applications. During the pyrolysis were evaluated the effect of different temperatures (400, 500, 700 and 800 °C) on the physicochemical characteristics of the AC. The activation step was realized under flow of 150 ml min⁻¹ of carbon dioxide (CO₂), at 800 °C for 2 hours, using a heating ramp of 10 °C min⁻¹. The activated carbons were characterized by nitrogen adsorption isotherms (77 K), FTIR and point of zero charge (PZC). It was possible to obtain microporous adsorbents with specific area ranging between 300 and 410 m².g⁻¹. The materials proved hydrophobic and basic superficial character (PZC~9). It was observed that pyrolysis temperature does not significantly affect the characteristics of activated carbons obtained. The total yield for the activated carbon production ranged between 24 and 54%, decreasing with the increase of the pyrolysis temperature. In this way, the process can be conducted at 400 °C, achieving, thus, energy saving and higher total yields (54%). It was noted that an increase of the temperatures increases the liquid and gaseous yields and decreases the solid residue yield. The pyrolysis liquid showed an acidic character (pH = 1.0). The chemical composition of the bio-oil was analyzed by gas chromatography coupled to a mass spectrometer and were identified a great variety of compounds. Such composition suggests that the bio-oil from sugarcane bagasse pyrolysis is a promising source of components for chemical, nutritional and pharmaceutical use.

1. Introduction

The most immediate application of bagasse generated by industries that produce ethanol and sugar in Brazil is as fuel for heating water boilers; it consumes 60-90% of the total bagasse generated. One possibility of using this residue is the production of activate carbon (AC), which is an efficient adsorbent, and bio oil.

In a physical activation process the lignocellulosic precursor is subjected to a pyrolysis under an inert atmosphere, and the resulting char with a small adsorption capacity is subjected to a partial and controlled gasification at high temperature with steam, carbon dioxide, air, or a mixture of these (Rodríguez-Reinoso and Molina-Sabio, 1992).

When using CO₂ as activating agent the process may be considered more clean and easy handling. Another advantage of using CO₂ is the ease of control of the activation process due to the slow reaction speed at temperatures around 800 °C (Zhang et al., 2004). According Aworn et al. (2008) this reaction is endothermic and acts removing carbon atoms of the solid matrix forming the pores of the adsorbent, according to Eq(1).



The pyrolysis process is an efficient way of recovering energy by generating carbon, bio-oil and gaseous products. Thus, the aims of this work were to prepare activated carbon and bio oil from sugarcane bagasse by a physical activation process (CO_2) and evaluate their physicochemical characteristics.

2. Experimental

2.1 Materials

The sugarcane bagasse used in this study was provided by the industry that produces ethanol and sugar in Brazil. This biomass was used as received without prior pretreatment. After collection, the bagasse was dried in an air circulation oven at 60 °C for 24 h and stored in plastic bags until the use. Then the material was screened, using for working the retained fraction between 5.61 and 0.99 mm.

2.2 Methods

2.2.1 Preparation and characterization of activated carbon

The preparation process of activated carbon consists of two steps: a preliminary pyrolysis followed by physical activation (CO_2). During the pyrolysis were evaluated the effect of different temperatures (400, 500, 700 and 800 °C) on the physicochemical characteristics of activated carbon. The method consists in the pyrolysis of sugarcane bagasse conducted in a stainless steel reactor, which was inserted into a tube furnace with a temperature controller and input to gas flows. The components of the experimental unit are schematized in Figure 1. The material was subjected to pyrolysis under a nitrogen flow (150 ml min⁻¹) with a heating ramp of 10 °C min⁻¹ for level 2 h, at different temperatures: 400, 500, 700 and 800 °C. Subsequently, 5 g of the pyrolysed carbon sample were subjected to activation under a flow of 150 mL min⁻¹ of carbon dioxide (CO_2) at 800 °C, with a 10 °C min⁻¹ heating ramp for level 2 h. A single experimental test for each condition were performed. The carbon mass yield of pyrolysis (Y_P) was calculated according to Eq(2).

$$Y_P(\%) = \left(\frac{m_C}{m_{Initial}} \right) \times 100 \quad (2)$$

Where: m_C means the mass of carbon obtained in the bagasse pyrolysis and $m_{Initial}$ means the initial mass of sugarcane bagasse.

The subsequent activation step was realized under flow of 150 ml min⁻¹ of carbon dioxide (CO_2), at 800 °C for 2 hours, using a heating ramp of 10 °C min⁻¹.

The Burn-off and the total yield (Y_T) of the process were calculated according to Eq(3) and Eq(4), respectively.

$$\text{Burn - off (\%)} = \left(\frac{m_C - m_{AC}}{m_{Initial}} \right) \times 100 \quad (3)$$

$$Y_T(\%) = \left(\frac{Y_P (100 - \text{Burn - off})}{100} \right) \quad (4)$$

The activated carbons were characterized by nitrogen adsorption isotherms (77 K) (Quantachrome, NOVA-1200 model). The specific area of the materials was estimated by the BET method. The areas of meso (S_{Meso}) and micropores (S_{Micro}) were determined by t-plot and BJH methods, respectively, and the average pore radius (r) was calculated by the BJH method.

The point of zero charge (PZC) of activated carbon samples were performed according to the methodology described by Regalbuto and Robles (2004).

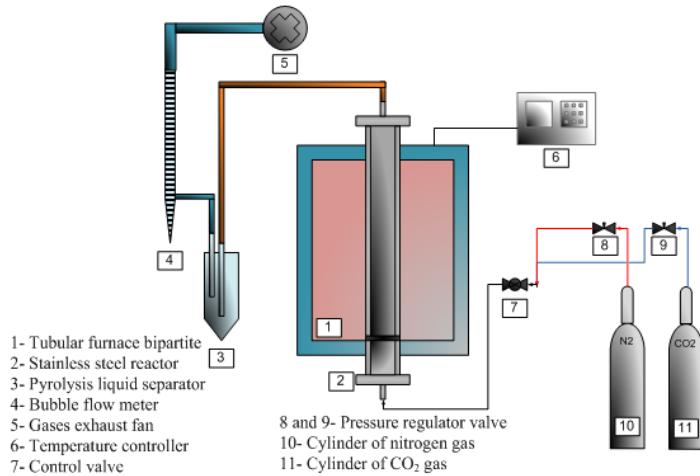


Figure 1: Layout of the experimental unit for preparing of the AC.

2.2.3 Characterization of pyrolysis liquid

During the pyrolysis, besides the carbon was collected in a condenser (room temperature) the liquid freed from biomass. The mass yield of the pyrolysis liquid (Y_{PL}) was determined relative to the initial mass of sugarcane bagasse ($m_{Initial}$) according to Eq(5).

$$Y_{PL} (\%) = \left(\frac{m_{PL}}{m_{Initial}} \right) \times 100 \quad (5)$$

Where: m_{PL} means the mass of pyrolysis liquid obtained in the bagasse pyrolysis.

The water content of the pyrolysis liquid was determined by the Karl Fischer method according to ASTM D-1744 standard.

The pyrolysis liquid was separated into various fractions through the solubilization and separation with different polarities solvents (pentane, benzene, dichloromethane and ethyl acetate), according to methodology used by Garcia-Pérez et al. (2002). The soluble fractions thus obtained were called bio-oil. The chemical composition of bio-oil, fractionated in different solvents was analyzed by gas chromatography-mass spectra (GC-MS) according to the methodology described by Garcia-Pérez et al. (2002).

The samples were analyzed on a GC FOCUS equipment, of the mark Thermo Electron Corporation. 20 μL of the samples were heated in a thermostatic bath for 30 min at 90 °C. 0.5 ml of the sample obtained by manual headspace was analyzed. The separation was conducted using an Agilent column HP5-MS, 30 m long, 0.25 mm in diameter and thickness of film of 0.25 μm . The analysis was conducted with a heat ramp of 3 °C min^{-1} until 260 °C. The injector temperature was set at 270 °C using the Split mode with a ratio 1:20. The carrier gas used was helium with a flow rate of 1 mL min^{-1} . The final column was introduced directly into a mass detector DSQ II. The operation conditions were as follows: transfer line temperature of 270 °C and 70 eV. The data acquisition was performed with the help of the Xcalibur software.

3. Results and discussion

The evaluated activation process was efficient in obtaining adsorbent materials. The results of textural analysis for AC with CO₂ are shown in Table 1. The value of specific area for the different samples remained between 300 and 410 $\text{m}^2 \text{ g}^{-1}$. These results are in agreement with those obtained by Pendyal et al. (1999) who prepared granular AC using bagasse from sugarcane and molasses as an agglomerating agent. These authors obtained values for the specific area ranging from 247 to 455 $\text{m}^2 \text{ g}^{-1}$.

The N₂ adsorption isotherms obtained for the AC samples are shown in Figure 2. It is observed that the samples are typical of microporous materials having Type I isotherm, according to the IUPAC (1985) classification. It is also observed that the pyrolysis temperatures of 500 and 700 °C produce materials with higher surface areas.

Table 1: Physical and chemical properties of the activated carbons under different pyrolysis temperatures (400, 500, 700 and 800 °C).

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{Meso} ($\text{m}^2 \text{g}^{-1}$)	S_{Micro} ($\text{m}^2 \text{g}^{-1}$)	r (Å)	PZC
400 CO ₂	300	7.4	153	20	9.2
500 CO ₂	407	7.6	172	18	9.0
700 CO ₂	410	8.2	85	18	8.8
800 CO ₂	355	8.8	118	19	8.8

It is known that changes in the pH of solutions, between other factors, affect the surface charge of the AC, influencing the dissociation of active functional groups on the adsorbent surface. Then, surface affinity for positive charged pollutants as metal cations and/or for negative charged organic compounds will depend on the relation between pH of the solution and PZC. Thus, the PZC determination and the pH of the media will help to understand the possible adsorption mechanisms (Rodríguez-Díaz, 2015).

The PZC (values pH in which the charge density in the material surface is 0), shown in Table 1, did not differ significantly among the different treatments, showing an average value of 9. The value located in the basic range is in agreement with the high activation temperature used (800 °C). This means that the materials have mainly negative charges in the surface which offer a certain affinity for cations adsorption.

In addition, all the samples present a highly hydrophobic character. According to Moreno-Castilla (2004), usually an increase in oxygen content present in the carbon surface results in a decrease in their hydrophobicity, indicating that the activation process with CO₂ causes a reduction in concentration of oxygenated groups on AC, owing to the high activation temperature used (800 °C).

According to Ruthven, (1984) as the surface of activated carbon is essentially non-polar, this type of adsorbent tends to be hydrophobic and organophilic. Thus, it is mainly used for the adsorption of organic compounds, in the clarification sugar, water purification, solvent recovery systems and air purification.

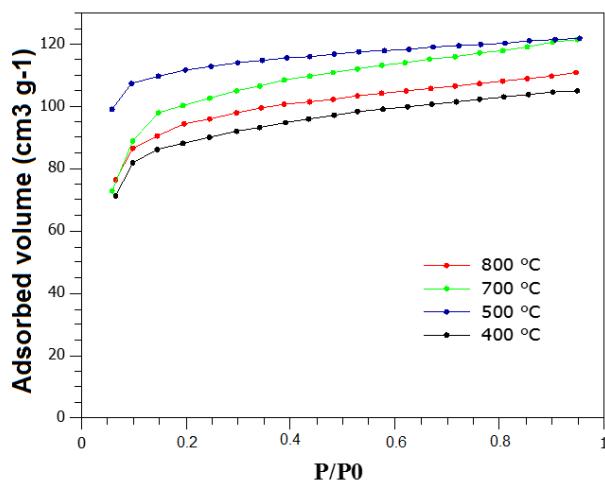


Figure 2: N_2 adsorption isotherm (77 K) for the AC under different pyrolysis temperatures (P = Measured pressure; P_0 = Initial pressure).

The total yield for the activated carbon production ranged between 24% wt and 54% wt, decreasing with the increase of the pyrolysis temperature. The best condition found in relation to the AC yield of the process was the pyrolysis temperature of 400 °C.

These results are in agreement with those obtained by Gonçalves et al. (2006). The authors prepared granular AC from sugarcane bagasse, agglomerated with different proportions of molasses, pyrolyzed at 850 °C for 1 h and activated with CO₂ for 30 min. The authors obtained average values of 17% wt for burn-off, 27% wt for the pyrolysis and 23% wt for the total yield.

It is possible to note that the yield of pyrolysis liquid increase with increasing temperature while AC yield decrease, indicating that higher temperatures favor decomposition of sugarcane bagasse in greater amount of volatile compounds (gases and bio-oil). Thus, the production process must be optimized depending on the product of interest: AC or bi-oil.

Table 2: Pyrolysis yield, burn-off grade, total yield and pyrolysis liquid yield for AC preparation according to the pyrolysis temperature of sugarcane bagasse.

Pyrolysis temperature (°C)	Pyrolysis yield (%)	Burn-off (%)	Total AC yield (Y_T) (%)	Pyrolysis liquid (Y_{PL}) (%)
400	81.8	33.6	54.32	24.03
500	39.2	23.4	30.06	33.76
600	32.0	11.6	28.29	34.50
700	32.8	10.8	29.26	35.41
800	26.0	8.14	23.88	41.28

The pH and water content of the liquid pyrolysis as a function of heat treatment temperature of sugarcane bagasse are shown in Table 3.

Table 3: Values of pH and water content for the pyrolysis liquid according to different temperatures.

	Pyrolysis temperature (°C)				
	400	500	600	700	800
pH	0.92	1.12	1.24	1.18	0.97
Water content (%)	90.3	89.5	86.7	84.3	82.6

Table 4: Chemical composition of bio-oil.

Components	Solvent extractant of each fraction			
	Ethyl Acetate	Benzene	Dichloromethane	Pentane
Acetic acid	x		x	x
Formate 3-Methyl-1-Butanol	x			
Pentanol	x			
Methyl ester	x			
d-glycero-d-galacto-heptose	x			
Hexanoic acid	x			
Benzene, 1,4-Bis (1,1-dimethylethyl)	(1,1-	x		
Benzenodiol, 2,6-bis (1,1-dimetil etil)		x		
2-Hexadecanol	x			x
Acetone		x	x	
Trimethylamine		x		
Methyl formate		x		
1-Hydroxy-2-Butanone		x	x	
Furfural		x		
Propionic acid		x	x	
1-acetyloxy-2-propanone		x		
4-Methyl-2-nitro-1,3-pantanediol		x		
Butanediol		x		
Furano		x	x	
Acetaldehyde		x		
Aminoguanidine			x	
1-Hydroxy-2-propanone			x	
Methyl ethyl ketone			x	
Phenol			x	
Ethyl acetate				x
Methyl propionate				x
1-Chloro octadecane				x
Cyclohexasiloxane, decamethyl				x

The pyrolysis liquid obtained presented a yellowish color and odor of smoke. For pyrolysis temperature of 400 °C the sample appeared in the form of a homogeneous emulsion, indicating the presence of a large amount of water (90.3%). These values are in agreement with those obtained by Asadullah et al. (2007), according to these authors, pyrolysis liquid can be considered a micro-emulsion wherein the continuous phase

is an aqueous solution of decomposition products of the holocellulose. This phase would stabilize the discontinuous phase of lignin macromolecules through mechanisms such as hydrogen bonding.

Already for the samples treated at 500, 600, 700 and 800 °C was observed phase separation with the presence of bio-oil droplets.

Furthermore, the pyrolysis liquid presented an acidic nature, with pH around 1.0, with no significant differences in relation to temperature variations. The acidity is mainly due to the presence of low molecular weight carboxylic acids.

The list containing the major components of bio-oil fractions are presented in Table 4. Note the wide range of compounds identified. According to Garcia-Pérez et al. (2002), this chemical composition suggests that the bio-oil from pyrolysis bagasse is a promising source of components for chemical, nutritional and pharmaceutical use. According to Fisher et al. (2002) the primary decomposition of biomass takes place at temperatures under 400 °C. At temperatures above this there is a secondary decomposition processes involving the aromatization components. It is observed then the presence of aromatic compounds such as phenol and benzenediol in the bio-oil.

According Yaman (2004) the presence of acetic acid is derived from acetyl groups from hemicellulose. Note also, by the sharp odor of acetic acid presented by bio-oil that this component is present in high proportion.

4 Conclusions

The possibility of producing activated carbon from sugarcane bagasse is promising since it is possible to add value to an important agro industrial waste. The preparation method evaluated in the present work has operational advantages when compared to chemical methods, once finished the pyrolysis step of the raw material, the N₂ flow can be easily changed by the CO₂ flow and the activation step to be conducted subsequently without removal of the sample inside the reactor. Therefore, it was possible to obtain microporous adsorbents with specific area ranging between 300 and 410 m² g⁻¹. In addition, the materials proved hydrophobic and basic superficial character. It was observed that pyrolysis temperature does not significantly affect the characteristics of activated carbons obtained. In this way, the process can be conducted at 400 °C, achieving, thus, energy saving and higher total yields (54% wt). Furthermore, it is possible to simultaneously obtain bio-oil, a material which can be used as fuel or as a source of various chemical compounds.

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