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Potentialities of the Biochar Generated from Raw and Acid Pre-Treated Sugarcane Agricultural Wastes

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ABSTRACT

Physico-chemical properties and yield of the biochar arising from slow pyrolysis of raw agricultural wastes from sugarcane (*Saccharum officinarum*) at two different temperatures (600 °C and 800 °C) are ascertained in order to evaluate potentialities for specific end-uses. According to international indicators, the biochar derived at both temperatures has potentiality as solid bio-fuel for domestic use, whereas only the biochar produced at the higher temperature might be employed for briquettes manufacture and/or in the steel industry. Textural characteristics of the biochar generated at the higher temperature also indicate that it is reasonably suited for potential use as low-cost rough adsorbent, soil amender, and/ or for further conversion into activated carbon. Besides, textural features and yield of the biochar obtained at the lower temperature are compared with those determined for the one generated from pyrolysis of the wastes pre-treated with a phosphoric acid solution under similar operating conditions. The acid treatment induces an enhanced yield and a highly developed porous structure of the biochar whose textural features are comparable to those of commercially available activated carbons. Accordingly, the biochar derived from the acid-pretreated sugarcane agricultural wastes could be a convenient substitute of conventional activated carbons extensively used in sugar manufacture and related industries.

Keywords: sugarcane agricultural wastes, biochar properties, pyrolysis, biofuel, activated carbon

1. INTRODUCTION

Sugarcane (*Saccharum officinarum*), the world's largest agricultural crop, has been traditionally cultivated as the main source of sugar in several regions worldwide, on which some economies still rely. Over 1200 sugarcane factories in 80 countries grind and process nearly 800 Mt of sugarcane [1-2]. Industrial processing of sugarcane yields quantities of bagasse arising as waste product after extraction of the sugar juice. In addition to bagasse, copious amounts of agricultural wastes from sugarcane are generated when the plant's stems are cleaned in the conditioning-stage for further industrial processing towards sugar. These wastes, mostly composed of leaves and tops, remain usually unused, despite they represent an attractive, abundant biomass resource. They are often stockpiled, landfilled, and /or open field burnt, affecting detrimentally the environment. In some countries, sugarcanes are cleaned in conditioning centers and therefore, gathering of agricultural residues should not involve additional costs [3]. Accordingly, thermochemical conversion of these residues into useful products by slow pyrolysis may represent an attractive option for its utilization since the process is relatively easy to carry out and does not require highly complex equipment [4].

Though thermochemical conversion of sugarcane bagasse has received great attention, effective utilization of sugarcane agricultural wastes as biomass feedstock has been scarcely explored. In particular, properties of the biochar, namely the enriched carbon solid product arising from biomass pyrolysis, are highly dependent on the feedstock and process conditions used. Within this context, the present work aims at characterizing the biochar produced by slow pyrolysis of sugarcane agricultural wastes (SAW) at two different temperatures (600 ºC and 800 ºC), in order to examine potentialities for specific end-uses. Besides, since pyrolysis of lignocellulosic biomasses pre-treated with phosphoric acid solutions has demonstrated to yield solid products with well-developed porous structures as those of activated carbon and accounting for the major use of this adsorbent in sugar manufacture, yield and textural features of the biochar arising from pyrolysis of the acid-pretreated agricultural wastes at the lower temperature are also investigated.

2. EXPERIMENTAL SECTION

Pre-dried agricultural wastes from sugarcane (*Saccharum officinarum*), composed of leaves and tops, were supplied by a sugar factory located in Northwestern Argentine. The samples were dried, ground, milled, and screen-sieved. Fractions of 0.75 mm average particle diameter were selected to obtain biochar samples, whereas those of particle diameter below 250 µm were reserved for physico-chemical characterization and thermogravimetric analysis.

Two sets of slow pyrolysis experiments were performed in a bench-scale installation for preparation of the biochar. On one hand, pre-weighed samples of the raw agricultural wastes were subjected to pyrolysis under flowing N_2 (100 cm^3/min) in a stainless steel fixed-bed reactor. It was externally heated by an electric furnace commanded by a programmable temperature controller, which provided control of the heating rate, temperature, and heating time. The samples were thermally treated at a heating rate of 10 °C/min up to 600 °C and 800 °C, and held at these temperatures for 60 min. Afterward, they were cooled to room temperature keeping the N_2 flow, weighed, and stored in sealed containers for further characterization. Biochar samples obtained from the raw wastes at 600 ºC and 800 ºC are designated as RBIO600 and RBIO800, respectively.

On the other hand, samples of the wastes previously weighed were treated with a solution of analytical grade phosphoric acid (50 wt %). They were impregnated with a proper amount of the acid solution and left to soak for some hours. The acid-treated residues were subsequently pyrolyzed in the same equipment at 600 °C following a similar procedure as described above. After cooling, the resulting solid product was rinsed thoroughly with hot distilled water until the filtrate had a neutral pH, in order to remove the acid. It was then dried, and periodically weighed until constant weight was attained. The biochar obtained from the acid-pretreated wastes is denoted by ABIO600.Yields of all the derived biochars were calculated from weight differences.

Contents of the major constituent biopolymers composing the sugarcane agricultural wastes, *i.e* holocellulose (celullose + hemicellulose) and lignin, as well as solvent extractive components were determined according to TAPPI standard methods (T 204 om-88, T222 om-88). Proximate analyses of the wastes and of the biochar samples derived at the two temperatures (RBIO600, RBIO800) were carried out following ASTM standards. Their elemental compositions (C, H, N, S, and O, by difference) were assessed using a Carlo Erba EA 1108 analyzer. Higher heating value (HHV) of all these samples was determined using a Parr oxygen bomb calorimeter. Besides, the ash content of the biochar arising from pyrolysis of the acid-treated wastes was also determined.

Textural properties of the sugarcane agricultural wastes and of the biochar samples generated from the raw and acid-treated wastes were evaluated from N_2 adsorption measurements at (-196 °C) employing a surface area analyzer (Micromeritics Gemini 2360). N_2 adsorption isotherms were determined on the samples prior outgassed overnight at 120 °C under vacuum (10^{-6} mm Hg). They provide information about the presence of macropores, mesopores and larger micropores. Besides, surfaces of the raw wastes and of the biochar derived by pyrolysis of the acid-treated ones were examined by scanning electron microscopy (SEM) with a Philips XL - 30 Microscope.

Furthermore, in order to explore the influence of the acid treatment on the pyrolytic behavior of the SAW, non-isothermal thermogravimetric analysis was applied. Measurements for the raw and acid-treated agricultural wastes from room temperature up to 800 °C were performed. A thermogravimetric balance (Netzsch STA 409) equipped with a N_2 flow device and a data acquisition system was employed. The experimental runs were conducted using sample masses of 10 mg, a heating rate of 10 °C/min and a N_2 flow rate of 100 cm^3/min. Further details of the different procedures employed may be found elsewhere [5-6].

3. RESULTS AND DISCUSSION

Table 1 reports results from proximate and elemental analyses for the sugarcane agricultural wastes and biochar samples derived from the raw wastes at both temperatures. Contents of the major biopolymers composing the wastes and higher heating values are also included in the table.

Compared to data reported for sugarcane bagasse [3], the sugarcane agricultural wastes possess a lower content of volatile matter and larger ash amount. No sulfur was detected. As expected, pyrolysis promoted substantial changes in the wastes' composition, that depend on temperature and are reflected in chemical characteristics of the biochars. Variations are in accordance with general trends reported for lignocellulosic materials [5-6]. Release of volatile matter leads to enhancements in %C and in the inorganic material of the resulting biochars, even though the biochar obtained at both temperatures has almost the same ash amount. In addition, it should be mentioned that ash content for the biochar generated from pyrolysis of the phosphoric acid-treated wastes was somewhat larger than for the one obtained from the raw wastes at the same temperature. This is likely due to the formation of phosphor compounds poorly soluble in water that might remain in the resulting solid product after washing [7].

HHV of the raw agricultural wastes are rather lower than that reported for sugarcane bagasse [3], due to the smaller %C and larger ash content of the former one. However, the HHV for the biochar derived at 800 ºC is comparable to others determined from sugarcane bagasse for similar operating conditions. Experimental HHV of the sugarcane agricultural wastes and derived biochar are also in good agreement with those estimated by a multivariate unified correlation reported in the literature, that is based on elemental composition and ash content of the samples [8]. Although the SAW-derived biochars have lower HHV than those obtained from conventional wood feedstock, they are comparable to charcoal obtained from other agricultural and agro-industrial by-products [3, 5-6].

Table 1: Chemical Characteristics and Higher Heating Value of the Sugarcane Agricultural Wastes (SAW) and of the Biochar Derived From the Raw Wastes at 600 °C (RBIO600) and 800 °C (RBIO800)

Sample / Characteristic	SAW	RBIO600	RBIO800
Proximate analysis[a] (wt %)			
Volatile matter	79.2	18.9	4.9
Ash	5.8	21.1	21.4
Fixed carbon[b]	15.0	60.0	73.7
Ultimate analysis[c] (wt %)			
Carbon	44.5	76.6	90.3
Hydrogen	5.3	2.1	0.7
Nitrogen	1.2	0.3	0.6
Oxygen[b]	49.0	21.0	8.4
Biopolymers content[d] (wt %)			
Lignin	31	-	-
Holocellulose (cellulose + hemicellulose)	69	-	-
Higher heating value[a] (MJ/kg)	15.1	18.5	22.2

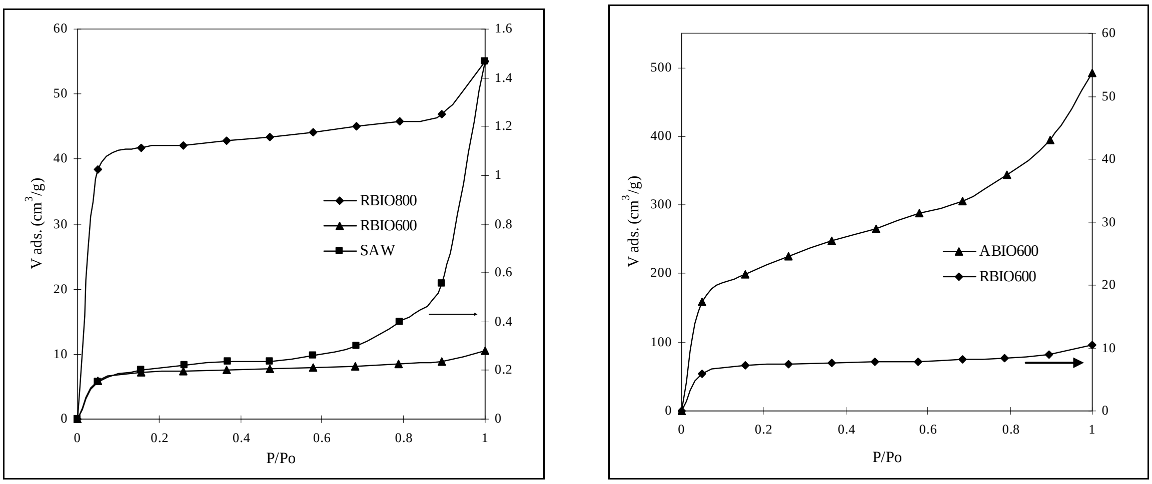
[a] Dry basis. [b] By difference. [c] Dry and ash free-basis. [d] Dry and extractive-free basis.

According to international standards reported in the literature [9], fixed carbon contents required for charcoal to be used in the manufacture of briquettes classified into A and B categories, prior to agglomeration, are 76±·3 (wt%) y 69±3 (wt%), respectively. Therefore, based on this requirement, only the biochar derived at the higher temperature has potential for this purpose. Another criterion adopted as an index of good quality takes into account volatile matter content of the char together with the intended application. For domestic use, volatile matter contents ranging between 20% and 30 % are acceptable, while these contents are restricted to 10-15% for use in the steel sector. Hence, both biochars might be employed for domestic uses, but only the one derived at 800 ºC is potentially suited for the steel sector.

Fig. 1(a-b) illustrates comparatively typical N_2 adsorption isotherms for the sugarcane agricultural wastes and the biochar samples derived from both the raw and acid-treated wastes. N_2 volumes adsorbed at standard temperature and pressure conditions per sample mass unit (Vads) are represented as a function of the relative pressure (P/P_0) in both figures. P and P_0 are the equilibrium and saturation pressures of the adsorbate, respectively.

As seen in Fig. 1a, N_2 volumes adsorbed on the biochars were pronouncedly higher than those on the wastes over the whole range of relative pressures. They indicate that pyrolysis induced creation of pores and/or opening up of pre-existent porosity, that seems to facilitate the access of N_2. The effect is more pronounced at the higher temperature likely due to the enhanced release of volatiles. The isotherms for the biochars also show different shapes compared to the agricultural wastes. The extensive plateau for the biochar obtained at 600 ºC is characteristic of Type I – isotherms according to IUPAC classification, pointing to a dominant presence of micropores. The isotherm of the biochar derived at 800 ºC exhibits some features of type II-isotherms. Comparison of N_2 isotherms for the biochars generated from pyrolysis of the raw and acid-treated stems at 600 °C (Fig. 1b) indicates a remarked enhancement in the developed porous structure for the biochar derived from the acid-treated wastes. Likewise, noticeable changes in the shape of the isotherms can be appreciated, suggesting that the acid pre-treatment of the wastes promotes development of larger size pores.

The Brunauer-Emmet and Teller (BET) model was applied to fit N_2 adsorption isotherms and evaluate the specific surface area of all the samples following the conventional procedure. Total pore volumes were determined from the amount of N_2 adsorbed on each sample at the highest relative pressure ($P/P_0 \cong 0.99$).



(a) (b)

Figure 1. N_2 (-196 °C) Adsorption Isotherms for: (a) Sugarcane Agricultural Wastes (SAW) and the Biochars Obtained from Pyrolysis of the Raw Wastes at 600 ºC (RBIO600) and at 800 ºC (RBIO800); (b) the Biochar Generated from Pyrolysis of Acid-Treated Sugarcane Agricultural Wastes at 600 °C (ABIO600).

Contribution of micropores to the total pore volume was estimated by applying the Dubinin-Radushkevich equation to the adsorption isotherms, whereas the mean pore radius (R) was calculated from $R = 2\ V_T/S_{BET}$. Surface properties of the wastes and derived biochars, as estimated from the corresponding isotherms, are reported in Table 2.

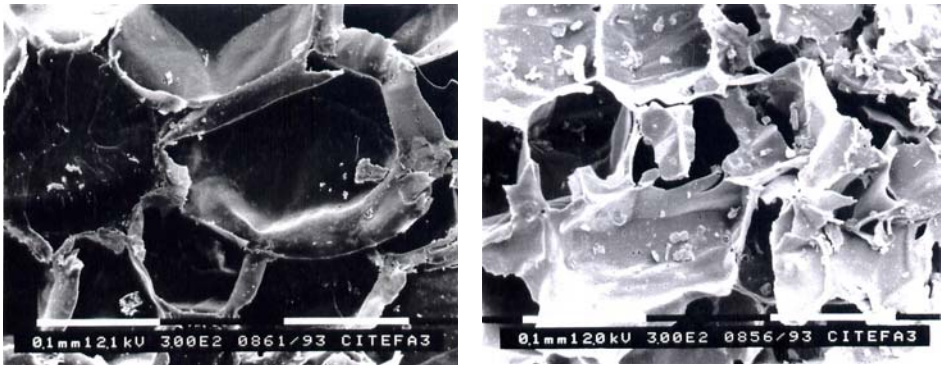
Table 2: Textural Characteristics of the Sugarcane Agricultural Wastes and of the Biochar Generated from Slow Pyrolysis of the Raw And Acid-Treated Wastes

Sample / Property	SAW	RBIO600	RBIO800	ABIO600
BET surface area (m^2/g)	0.7	21	135	740
Total pore volume (cm^3/g)	2×10^{-3}	2×10^{-2}	9×10^{-2}	8×10^{-1}
Micropore volume (%)	2	81	79	51
Mean pore radius (nm)	5.7	1.5	1.3	2.2

The three biochars exhibit larger BET surface areas and total pore volumes than the sugarcane agricultural wastes. Nevertheless, the differences are one order of magnitude greater for the biochar derived from the acid-treated wastes (ABIO600). For the raw wastes-derived biochars, pronounced reduction in the mean pore radius and increases in micropore volumes point to development of pore structures with predominant presence of micropores, in agreement with results reported for biochar obtained from other biomasses [5-6]. Textural properties of the RBIO800 indicate that it could be used as low-cost, rough adsorbent and/or soil amender to improve soil physical properties, such as texture, permeability, and water holding capacity [4].

Besides, as inferred from results in Table 2 for the ABIO600, the acid pre-treatment seems to promote development of a more open structure in the resulting biochar. Enhancement in BET area and pore volume for the biochar from the acid-treated wastes in comparison with that derived from the raw wastes (RBIO600) reveals a crucial role of the acid pre-treatment in the development of the porous structure. It leads to a biochar with textural properties similar to those of commercial activated carbons of fairly good quality. In this sense, the major use of activated carbons in sugar manufacture should be highlighted. The treatment of the sugar liquor with this adsorbent efficiently removes several coloured compounds. It is also used for decolorization of molasses wastewater, generating environmental problems in sugar and fermentation industries.

Fig. 3 (a-b) illustrates comparatively typical SEM micrographs of the surfaces of the sugarcane agricultural wastes and of the biochar obtained from the acid-treated wastes (ABIO600). The structure of the former shows flattened, polygonal-shaped cells of various sizes arranged in a honeycomb-like pattern (Fig. 3a). As seen in Fig. 3b, the acid treatment and subsequent pyrolysis of the wastes lead to modifications and opening of the structure which also shows some signs of structural weakness. Nevertheless, in spite of the changes, the original morphology of the wastes is quite preserved.



(a) (b)

Figure 3. SEM Micrographs (x 300) of the Surface of: a) Raw Sugarcane Agricultural Wastes; b) Biochar Produced from the Pyrolysis of the Acid-Treated Wastes at 600 ºC.

According to reported mechanisms, insertion of phosphate groups brings about stabilizing formation of bio-phosphate ester cross-links and a dilation process, that seem to be responsible for the extensive development of porosity. The phosphate linkages appear to give rise to a rigid, cross-linked structure, which restricts shrinkage and release of volatile matter. Dilation leaves the structure in an expanded state with an accessible highly developed porous matrix after acid removal upon washing [6-7].

As shown in Fig. 4, the acid pre-treatment of the sugarcane agricultural wastes also promotes a significant increase in biochar yield. Thermogravimetric (TG) analysis conducted for the pyrolysis of the raw and H_3PO_4 acid-treated wastes under flowing N_2 also supports the found trend.

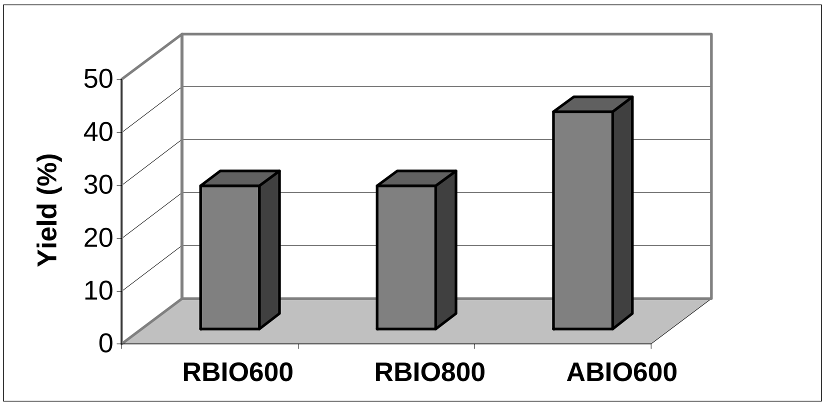
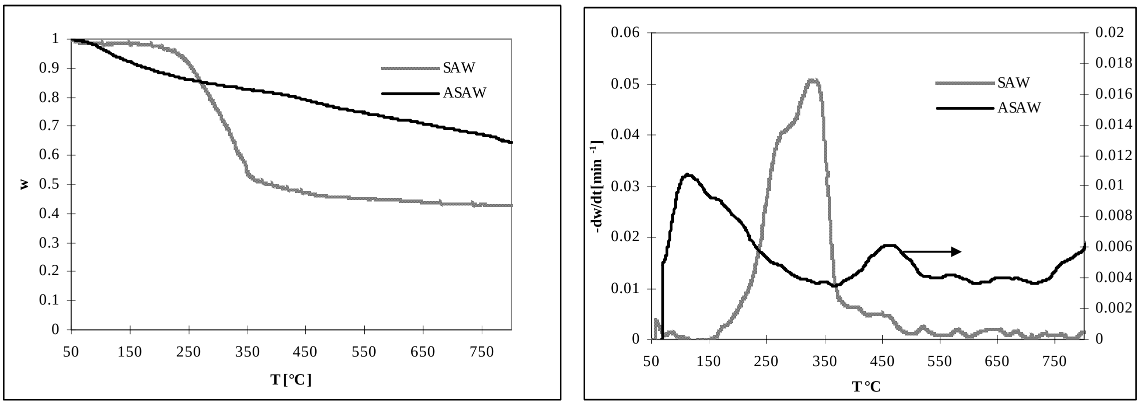


Figure 4. Yields of the Biochar Produced from the Raw Sugarcane Agricultural Wastes at 600 ºC and 800 ºC (RBIO600, RBIO800), and of the Biochar from the Acid-Pretreated Wastes at 600 ºC (ABIO600).

Typical TG curves and pyrolysis rate profiles are illustrated in Fig. 5 (a-b). Fig. 5a shows weight fraction (W) losses as a function of temperature (T). The pyrolysis rate profiles in Fig. 5b were obtained by differentiation of weight fractions vs time curves for each sample. As observed, pyrolysis of the raw wastes begins at around 200 °C proceeding through a sharp weight loss between 250 °C and 350 °C. For the acid-treated wastes, pyrolysis takes place steadily almost throughout the whole range of temperatures, including the low temperature region (< 250 °C) where no weight losses for the raw wastes are recorded. For temperatures higher than 300 ºC, weight fractions for the pyrolysis of the acid-treated wastes attain higher values than those for the untreated ones. At 600 ºC, values of $w = 0.42$ and $w = 0.75$ characterize pyrolysis of the raw and acid-treated wastes, respectively, in agreement with the trend for the yields shown in Fig. 4. Maximum pyrolysis rate for the raw wastes occurs at 300 ºC, while it shifts to lower temperatures (~ 150 ºC) and attains a lower value for the acid-treated ones. Seemingly, the acid acts a catalyst promoting bond-cleavage reactions, i.e. dehydration and depolymerization of the wastes, and redistribution of constituent biopolymers fragments that favor conversion of aliphatic to aromatic compounds at lower temperatures than for pyrolysis in the absence of the reagent, thus increasing the biochar yield. A similar behavior has been reported for other lignocellulosic samples [6-7].



(a) (b)

Figure 5. a) Thermogravimetric Curves for the Pyrolysis of the Raw and Acid-Treated Sugarcane Agricultural Wastes under Flowing N_2: Weight Fraction (W) as a Function of Pyrolysis Temperature (T); b) Pyrolysis Rate Profiles for the Raw and Acid-Treated Sugarcane Agricultural Wastes (SAW, ASAW).

CONCLUSIONS

Chemical, thermal, and textural characteristics of the biochar generated from pyrolysis of sugarcane agricultural wastes at 600 ºC and 800 ºC have been ascertained in an attempt to examine specific end-uses for this abundant biomass. Present results indicate that the biochar produced at both temperatures is potentially suited as bio-fuel for domestic use, whereas the one derived at 800 ºC could also be used for briquettes manufacture and in the steel sector as well as a low-cost, rough adsorbent, and/or soil amender.

Besides, pyrolysis of the wastes pre-treated with a phosphoric acid solution at the lower temperature leads to enhance the biochar yield (41%) and to a highly developed porous structure with textural properties (BET area ~ 750 m^2/g and total pore volume of about 1 cm^3/g), comparable to those of some commercially available activated carbons. Noticeable changes induced by the acid pre-treatment seem to be due to the catalytic action of the acid on the pyrolytic behavior of the wastes, promoting degradation at lower temperatures compared to pyrolysis of the untreated ones. The biochar from the acid-pretreated sugarcane agricultural wastes is found potentially appropriate as a substitute of conventional activated carbons extensively used in the sugar factories and related industries.

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