

Carbon sequestration as a profitable application for biomass pyrolysis solid products

V. Gargiulo¹, C. O. Ania², A. Gomis-Berenguer², P. Giudicianni¹, R. Ragucci¹, M. Alfe¹

1. *Istituto di Ricerche sulla Combustione - C.N.R., Napoli - Italy*

2. *CEMHTI (UPR 3079, CNRS), University of Orleans, 45071 Orleans- France*

Abstract

The presence of CO, CO₂, SO₂, NH₃ and volatile organic compounds (VOCs) in combustion exhaust is one of the main environmental concerns related to smart energy carriers (SECs) combustion, posing as a priority issue the monitoring of pollutants emissions in SECs combustion. Separation and quantification of pollutants from gas exhaust is inevitably demanded in order to minimize the impact of SECs combustion.

Adsorption techniques are a reliable diagnostic tool from both the technological and economical points of view (high energy efficiency, ease of control, low capital investment costs) to explore the fate of gases emitted to the atmosphere in various energy conversion processes (i.e., CO₂, CH₄, CO, H₂ among others). Adsorption on solid matrix represents a well-assessed method for the separation and quantification of CO₂ from gas exhausts [1-2]. An ideal CO₂ adsorbent: i) should exhibit high selectivity toward CO₂ over N₂ and other exhaust components (CO, NH₃ and light hydrocarbons (i.e. CH₄)), ii) should be produced via inexpensive and low-energy consumption methods and by using renewable resources as precursors, iii) should exhibit flexible morphologies, pore structures and functionalities, and iv) should exhibit good mechanical properties to undergo repeated adsorption-desorption cycles [2,3]. Structural features are relevant in view of the adsorbent selection and optimization since for carbon-based adsorbent the main parameters governing both the CO₂ uptake capacity and selectivity at low CO₂ partial pressure and room temperature are micropore volume and size and chemical functionalization of the pores [3,4]. Some authors suggested that high CO₂ uptakes correspond to samples with high micropore volumes and pore diameter below 0.8 nm, but as reported in [4] some discrepancies in literature can be found on this point. In the framework of adsorbent selection and preparation, adsorbents derived from re-cycle and/or re-use of wastes are particularly welcome since the use of wastes as starting valued material for sorbent production is an alternative to their disposal. The development of technologies devoted to cost reduction by using lignocellulosic biomass wastes generated from agroindustrial processing is a hot research topic. Agroindustry annually generates enormous amounts of residues and their reduction by utilization might mitigate environmental pollution and increase energy savings. In particular, an environmentally friendly cycle can be imagined considering the thermochemical conversion of agricultural wastes for the production of values added products: liquid and gaseous products can be used as SECs while the solid can act as potential pollutant storage sink. Biochar is a stable microporous carbon-rich by-product produced through pyrolysis/carbonization of plant- and animal-based biomass and could represent a promising candidate for environmental remediation [5,6]. Aim of this work is to investigate the applicability of biochar in carbon sequestration area, also taking into account the great structural and compositional variability of biomasses after controlled thermal conversion (surface area, pore size distribution, ash content).

Cellulose fibers and *Populus nigra* (*P. nigra*) wood were treated at different temperatures between 500 and 700 °C in a steam assisted slow pyrolysis lab-scale plant [7], at a pressure of 5×10^5 Pa and a heating rate of 5 °C/min [8]. Steam was selected as pyrolyzing agent because it is able to perform a more efficient penetration of solid matter enhancing desorption, distillation and removal of volatiles [8]. Slow pyrolysis conditions (high residence time and low heating rate) were selected because during thermal treatment at low heating rates the biomass structure is preserved and the pore development is strictly correlated to the degree of devolatilization and to the formation of cracks inside the char matrix [8]. Mild thermal conditions were applied because at $T < 400$ °C the removal of a great amount of volatile matter generates sparse void volume regions giving rise to a macroporous structure along with a low BET surface; at $T > 500$ °C, the formation of cracks in the material lead to the development of micropores and mesopores resulting in a great increase in surface area and porosity; finally, at $T > 800$ °C the rearrangement of the structure provoked the micropore coalescence leading to lower values of surface area [8]. *P. nigra* was selected as feedstock, since it is among the faster-growing trees for short rotation coppice with an annual dry matter production of 17.8 Mg ha⁻¹ y⁻¹ [8]. Additionally, cellulose fibers were used as model feedstock, since cellulose is the most abundant component in *P. nigra* wood (55.4 wt% cellulose, 11.6 wt% lignin, 26.8 wt% hemicellulose) [8].

Various chemical treatments were applied to the prepared biochars, aiming at increasing the CO₂ uptake, as described elsewhere [9]. Briefly, the biochar obtained at 600 °C was treated in 5 M NaOH to remove the ashes (base-leaching), and decorated with NH₂ groups through a reaction with DETA after an oxidation step [9]. Both the pristine and modified biochars were fully characterized by different analytical techniques. A combined analysis of N₂ isotherms at 77 K and CO₂ isotherms at 273 K allowed a complete characterization of the textural properties of all the materials object of this study [4,10].

The gas storage ability of the obtained biochars towards gases of strategic impact (ca. CO₂, CH₄) was evaluated with volumetric analyzers at ambient temperature and atmospheric pressure. The analysis of gas adsorption isotherms at 298 K allowed the estimation of the gas uptake for selected biochar samples and the prediction of the adsorption of binary gas mixtures (ca. CO₂/CH₄, and CO₂/N₂) by applying the ideal adsorbed solution theory (IAST) [11].

All the investigated unmodified biochars (with the exception of the biochar from *P. nigra* wood pyrolyzed at 480 °C) were mainly microporous materials, with a small contribution of mesoporosity to the overall porous structure. In general, for the unmodified biochars, the surface area increased with the pyrolysis temperature (Fig. 1a, left panel). This was in agreement with the analysis of CO₂ isotherms at 273 K, indicating that the pyrolysis temperature favored the development of narrower micropores (Fig. 1b, right panel). The average micropore diameter obtained by the application of Stoekli–Ballerini equation [12] to the CO₂ adsorption isotherms at 273 K was 0.6 nm for all the biochars, regardless the precursor. These values were in line with micropore diameters exhibited by other carbon-based materials with good CO₂ adsorption capacities [13].

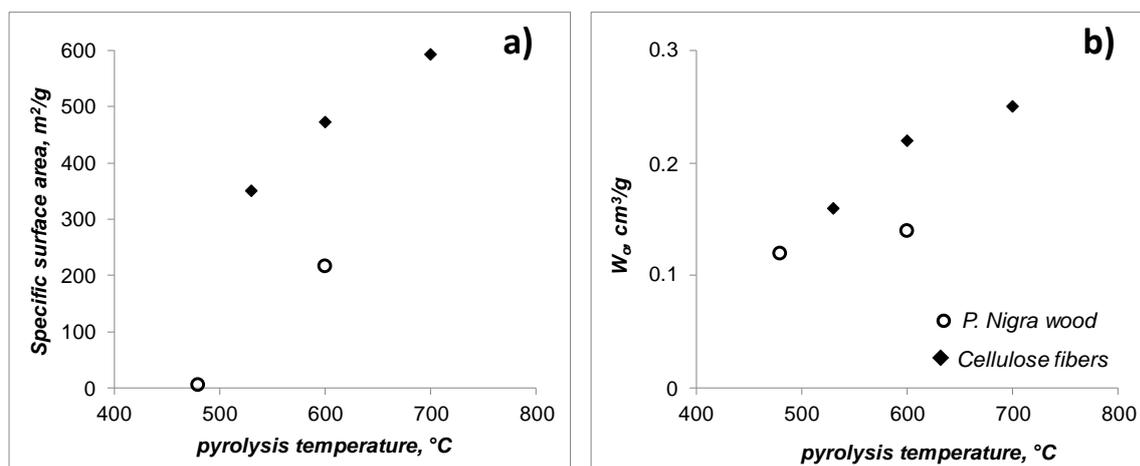


Fig. 1 BET specific surface area (a) and volume of narrow micropores W_0 (b) obtained from CO_2 adsorption isotherms, as function of pyrolysis temperature.

CO_2 adsorption capacity at 298 K was measured for a selection of samples, namely those with the highest micropore volumes: biochars from cellulose fibers pyrolyzed at 600 °C and 700 °C, biochar from *P. nigra* wood pyrolyzed at 600 °C and biochar from *P. nigra* wood pyrolyzed at 600 °C after ashes removal. CO_2 uptakes at 298 K and 1 bar of these samples ranged between 1-2.5 mmol/g; these values are not among the highest adsorption capacities reported for activated carbons [13,14], but yet are comparable to other carbon-based adsorbents reported in the literature [4,10]. A linear correlation was found between the narrow micropore volume (W_0) and the CO_2 uptake at 1 bar (Fig. 2). This corroborated the main role played by narrow micropores on the CO_2 adsorption at ambient conditions [13] and confirmed the suitability of the investigated biochars as CO_2 adsorbents.

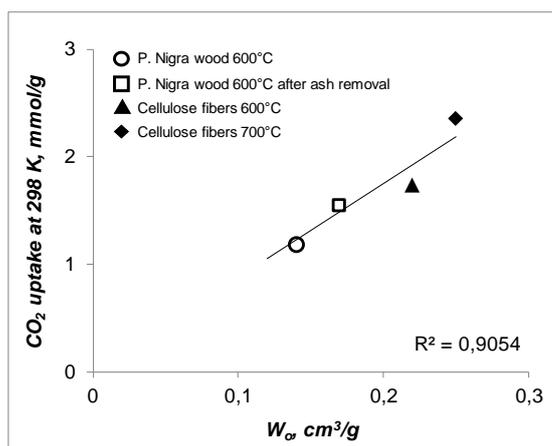


Fig. 2 Relationship between the experimental CO_2 adsorption capacity at 298 K and 1 bar and the narrow micropore volume, W_0 .

Among the investigated samples, the biochars prepared by the pyrolysis of cellulose fibers exhibited the highest sorption capacities and the highest CO_2/N_2 and CO_2/CH_4 selectivities. More specifically, the biochar obtained by the pyrolysis of cellulose fibers at 700 °C displayed the highest CO_2 uptake at 298 K and 1 bar (ca. 2.35 mmol/g), and the highest selectivity for CO_2 over N_2 in post-combustion conditions ($CO_2:N_2$ of 15:85, 298 K and 1 bar). The CO_2 uptake determined for this sample was comparable to that of cellulose fibers physically activated with steam at 700 °C (ca. 2.61 mmol/g) [14].

As for the chemical modifications of the biochars, data shown that the removal of the ash content did not significantly improved the CO₂ sorption capacity; the slight increase in the uptake (ca. 23%) was explained as the expected mass effect due to the partial removal of the no-adsorbing matrix (ashes). In the case of the NH₂-impregnated sample, a dramatic drop in the surface area drop was obtained (i.e., 7 vs 217 m²/g for the modified and pristine biochar, respectively) suggesting the occurrence of pore blockage effects. Despite of the drop in porosity, the uptake was quite large (i.e., 0.97 mmol/g at 1 bar), indicating that this is due to the interaction of CO₂ with NH₂ groups through chemisorption.

Summarizing, biochars produced from cellulose fibers and *P. nigra* wood under steam assisted slow pyrolysis conditions are microporous materials exhibiting CO₂ uptakes at 298 K similar to those of other carbonaceous materials reported in the literature. The samples also displayed a good selectivity against CO₂ over CH₄ and N₂. These results are promising also considering the added value of biochars that can be prepared by the valorization of highly available underutilized biomass residues.

References

- [1] S. Nanda, S.N. Reddy, S.K. Mitra J.A. Kozinski, *Energy Science and Engineering* 2016, 4(2):99-122;
- [2] D.M. D'Alessandro, B. Smit, J.R. Long, *Angewandte Chemie International Edition* 2012, 49:6058–6082;
- [3] C.F. Martin, M. G. Plaza, J.J. Pis, F. Rubiera, C. Pevida, T.A. Centeno, *Separation and purification technology* 2010, 74:225-229;
- [4] E.M. Calvo-Munoz, F.J. Garcia-Mateos, J.M. Rosas, J. Rodriguez-Mirasol, T. Cordero, *Frontiers in Materials*, 2016 3:23 (doi:10.3389/fmats.2016.00023);
- [5] M. Ahmad, A.U. Rajapaksha, J.E. Lim, *Chemosphere*, 2014 99:19-33;
- [6] J. Lehmann, J. Gaunt, M. Rondon, *Mitigation and Adaptation Strategies for Global Change* 2006, 11:403-427;
- [7] R. Ragucci, P. Giudicianni, A. Cavaliere, *Fuel* 2013, 107:122-130;
- [8] P. Giudicianni, S. Pindozzi, C.M. Grottola, F. Stanzione, S. Faugno, M. Fagnano, N. Fiorentino, R. Ragucci, *Waste Management* 2017, 61:288-299;
- [9] V. Gargiulo. M. Alfè, P. Ammendola, F. Raganati, R. Chirone, *Applied Surface Science* 2016, 360(Part A):329-337;
- [10] D. Lozano-Castello, D. Cazorla-Amoros, A. Linares-Solano, *Carbon* 2004, 42:1233-1242;
- [11] A.L. Myers, J.M. Prausnitz, *AIChE Journal* 1965, 11:121–127.
- [12] F. Rouquerol, J. Rouquerol, K.S.W. Sing, P. Llewellyn and G. Maurin "Adsorption by Powders and Porous Solids Principles, Methodology and Applications" Elsevier Science & Technology Books (ISBN: 978-0-08-097035-6), Second edition 2014;
- [13] S. Deng, H. Wei, T. Chen, B. Wang, J. Huang, G. Yu, *Chemical Engineering Journal* 2014, 253:46-54;
- [14] Y-J. Heo, S-J. Park, *Energy* 2015, 91:142-150.