Study of the Influence of Pyrolysis Conditions on the Textural Properties of Physically Activated Biochars

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Abstract

Nine wheat straw-derived biochars were produced under different pyrolysis conditions (i.e., peak temperature, absolute pressure, and pyrolysis atmosphere) and subsequentially activated with $\rm CO_2$ at 800 °C in order to study the influence of the pyrolysis operating conditions on the textural properties of the resulting activated biochars.

Background

Activated carbons are characterized for being highly porous materials with a large surface area. These structural features make such materials ideal for being used in several fields (e.g., energy production, gas cleaning and catalysis). The main drawback of the activated carbons is that their production usually involves expensive processes; arch discharge [1], vapor deposition [2], and carbonization of synthetic polymers [3] are some of them. A valid alternative is the use of "biochar", an organic charred solid obtained from the thermal degradation of biomass, as a promising precursor of advanced carbon materials. Although the low specific surface area and a pore size distribution dominated by narrow micropores, it is possible to enhance the biochar textural properties through an activation process, which can be carried out in different ways. One of the most promising activation methods is the so-called "physical activation", which consists in a controlled gasification of the solid, using CO2 as oxidizing agent. Despite the fact that numerous studies in the literature have focused on the correlation between the activation process parameters (e.g., temperature and soaking time) and the textural properties of the activated biochar [4,5], there is almost no research on how the pyrolysis process conditions, at which the biochar precursors are produced, can affect the porosity of the subsequent activated biochars. Therefore, the specific aim of this work is to evaluate how the slow pyrolysis process conditions adopted for the production of biochars from wheat straw pellets can affect the textural properties of the final activated carbons, which are obtained via physical

activation with CO_2 of the raw biochars. **Experimental section**

Wheat straw-derived biochar was produced using a bench-scale fixed bed reactor. Details about the device are available elsewhere [6]. Slow pyrolysis (at an average heating rate of 5 °C min⁻¹) was conducted under different combinations of absolute pressure, peak temperature and type of gas atmosphere during the process (see Table 1). The raw pellet-shaped biochars were then crushed and sieved to obtain particle sizes in the range of 0.212-1.41 mm. The activation was carried out in a fixed bed reactor, in which 20 g of biochar were placed and heated up to 800 °C with a heating rate of 10 °C min⁻¹, under N₂ atmosphere. After reaching the target temperature, the inlet gas stream was switched to pure CO₂ $(GHSV = 7000 h^{-1})$. The activating conditions were kept for 60 min after which the system was cooled down under N₂ atmosphere.

N₂ and CO₂ adsorption isotherms, performed at–196 °C and 0°C, respectively, were used to determine the specific surface area and pore size distribution of both raw and activated biochars.

Preliminary results

To date, all the biochar precursors have been produced and physically activated. The samples analyses, in terms of surface area and pore size distribution, are currently under progress.

Table 1. Pyrolysis operating conditions

Pyrolysis conditions			
#	Temperature	Abs. Pressure	Carrier gas
	(°C)	(MPa)	(vol _{N2} :vol _{CO2})
1	400	0.2	100:0
2	400	0.9	100:0
3	400	0.2	40:60
4	400	0.9	40:60
5	550	0.2	100:0
6	550	0.9	100:0
7	550	0.2	40:60
8	550	0.9	40:60
9	475	0.55	70:30

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References

[1] VOLOTSKOVA, O., LEVCHENKO, I., SHASHURIN, A., RAITSES, Y., OSTRIKOV, K. and KEIDAR, M. Single-step synthesis and magnetic separation of graphene and carbon nanotubes in arc discharge plasmas. In:

Nanoscale. 2010, 2 (10), 2281-2285.

- [2] LI, X., CAI, W., AN, J., KIM, S., NAH, J., YANG, D., PINER, R., VELAMAKANNI, A., JUNG, I., TUTUC, E., BANERJEE, S. K., COLOMBO, L. and RUOFF, R. S. Largearea synthesis of high-quality and uniform graphene films on copper foils. In: *Science*. 2009, 324 (5932), 1312-1314.
- [3] YANG, Z., SHEN, J., JAYAPRAKASH, N. and ARCHER, L. A.. Synthesis of organic-inorganic hybrids by miniemulsion polymerization and their application for electrochemical energy storage. In: *Energy and Environmental Science*. 2012, 5, 7025-7032.
- [4] AZARGOHAR, R. and DALAI, A. K. Steam and KOH activation of biochar: Experimental and modeling studies. In: *Microporous and Mesoporous Materials*. 2008, 110 (2-3), 413-421.
- [5] CHANG, C.F., CHANG, C.Y., and TSAI, W. T. Effects of burn-off and activation temperature on preparation of activated carbon from corn cob agrowaste by CO₂ and steam. In: *Journal of Colloid and Interface Science*. 2000, 232 (1), 45-49.
- [6] GRECO, G., VIDEGAIN, M., DI STASI, C., GONZÁLEZ, B. and MANYÀ, J.J. Evolution of the mass-loss rate during atmospheric and pressurized slow pyrolysis of wheat straw in a bench-scale reactor. In: *Journal of Analytical and Applied Pyrolysis*. 2018, 136, 18-26.