Supplementary Material

Adsorption performance of physically activated biochars for postcombustion CO_2 capture from dry and humid flue gas

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Proximate and ultimate analyses. Proximate analyses of the biomass sources (VS and WS) and activated biochars were performed in quadruplicate according to ASTM standards (D3173 for moisture, D3174 for ash, and D3175 for volatile matter). Ultimate (elemental) analyses were carried out using a combustion elemental analysis Leco CHN628 (Leco Corporation, USA).

Estimation of textural parameters of activated biochars. From the N_2 adsorption/desorption isotherms at −196 °C, the apparent specific surface area (S_{BET}) was calculated using the Brunauer–Emmet–Teller (BET) model at small relative pressures (p/p^0 = 0.01–0.10). A Non-Local Density Functional Theory (NLDFT) method assuming slit-pore geometry was used to estimate the Pore Size Distribution (PSD) for pore sizes above 0.9–1.0 nm and the micropore and mesopores volumes (V_{mic} and V_{mes}, respectively).

Narrow micropore size distributions (up to 0.8–0.9 nm) and the volume of ultra-micropores (V_{ultra}, for pore sizes lower than 0.7 nm) of activated carbons were estimated from their CO_2 adsorption isotherms at 0 °C. A Density Functional Theory (DFT) method assuming slit-pore geometry was employed.

All the calculations were performed using the MicroActive software (v. 4.03) supplied by Micromeritics (USA).

Determination of key performance indicators from dry breakthrough experiments. First, the experimental breakthrough curves were corrected by subtracting the dead time, which was previously estimated from the blank tests. From the corrected curves, the volumetric flows of CO_2 and N_2 at the outlet were calculated as follows:

$$\dot{V} = \dot{V}_{N2} + \left(\frac{1}{F_{CO2}} \right) \dot{V}_{CO2} \tag{A.1}$$

$$y_{CO2} = \frac{\dot{V}_{CO2}}{(\dot{V}_{CO2} + \dot{V}_{N2})} \tag{A.2}$$

where $\dot{V}$ is the total volumetric flow rate (at STP conditions) at the outlet of the adsorption column (which is continuously measured using a mass flow meter, as shown in Fig. 1), whereas $\dot{V}_{CO2}$ and $\dot{V}_{N2}$ correspond to the outlet volumetric flow rates of CO_2 and N_2, respectively. Since the mass flow meter used here was calibrated for pure N_2, a correction factor (F_{CO2} = 0.74) was applied for quantifying $\dot{V}_{CO2}$. The analyzer from ABB (see Section 2.3) continuously monitored the outlet composition of CO_2 in molar fraction (y_{CO2}).

Once the outlet volumetric flow rates of both CO_2 and N_2 were determined, the specific adsorption amounts (q_i, in mmol g^{-1}) for each gas were estimated through the following equations:

$$q_{CO2} = \frac{1}{m_b} \left[\int_0^{t_s} (\dot{V}_{IN,CO2} - \dot{V}_{CO2}) \frac{1}{22.4} dt - \frac{P y_{CO2} \varepsilon V_b}{RT} \right] \tag{A.3}$$

$$q_{N2} = \frac{1}{m_b} \left[\int_0^{t_s} (\dot{V}_{IN,N2} - \dot{V}_{N2}) \frac{1}{22.4} dt - \frac{P(1 - y_{CO2}) \varepsilon V_b}{RT} \right] \tag{A.4}$$

where m_b is the mass of adsorbent in g, $\dot{V}_{IN,i}$ corresponds to the inlet volumetric flow rate (at STP conditions, $cm^3\ s^{-1}$) of gas constituent *i*, and t_s is the time required to reach the CO_2 concentration in the feed (i.e., C/C_0 =1). Eqs. (S3) and (S4) contain correction terms that account for the gas trapped in the void fraction of the bed (*P*: absolute pressure, ε: porosity of the bed, V_b: total volume of the bed, *T*: adsorption temperature).

The breakthrough time (t_b) was defined as the time elapsed from the beginning of the adsorption and the instant at which CO_2 was detected in the outlet stream. Hence, the percentage of used bed was determined from the ratio of the specific CO_2 uptake at t_b to that obtained at t_s. The experimental values of selectivity CO_2/N_2 were calculated as follows:

$$S = \frac{q_{CO_2}\,(P - p_{CO_2})}{q_{N_2}\,p_{CO_2}} \tag{A.5}$$

where q_{CO2} and q_{N2} correspond to the adsorption capacities determined using Eqs. (A.3) and (A.4), respectively.

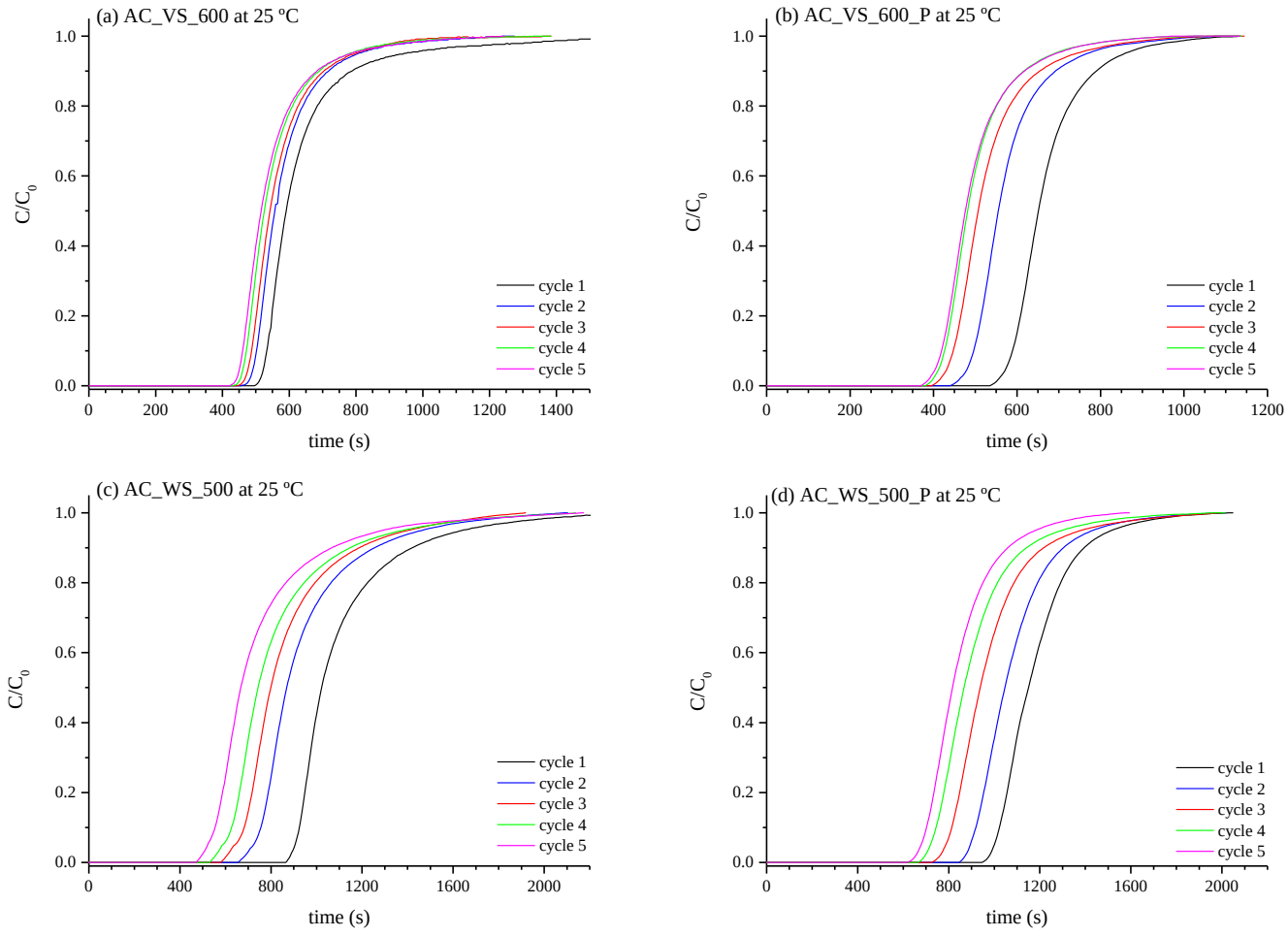

Figure A.1. CO_2 breakthrough curves for five consecutive cycles (adsorption temperature = 25 °C) from a dry binary mixture of N_2 and CO_2 (with a CO_2 composition of 13.75–14.25 vol. %).