Supplementary Materials: Non-Energy Valorization of Residual Biomasses via HTC: CO_2 Capture onto Activated Hydrochars

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BET-BJH analysis

A NOVA 1200e Alfates Quartachrome surface area and porosity analyser records N_2 adsorption and desorption isotherms at N_2 boiling point -196 °C and performs calculations by BET and BJH methods with Quantachrome Instruments version 11.0.

Samples consist of 50-100 mg of powder (average size of the powder between 106 μm and 355 μm). Degassing of the powder is performed before the analysis under a high vacuum, with 10 °C min-1 heating ramp until 100 °C and dwell of 3 h.

Considered measures are BET surface area (A_{BET}), BJH cumulative pore volumes (V_{BJH}), BJH pore volume distributions with respect to pore sizes, and BJH averaged cylindrical pore diameter ($D_{av,BJH}$). BET isotherms assume that:

- the heat adsorbed by the first layer is constant;
- the interaction between adsorbed molecules in the same layer can be neglected;
- the adsorbed molecule can form a new absorbing surface making the process continuous;
- the heat of adsorption for all other layers, after the first, is equal to the heat of liquefaction.

For the determination of SBET the BET isotherm in linear form (Equation S1) is commonly used:

$$\frac{P/P_0}{n(1-P/P_0)} = \frac{1}{n_m C} + \frac{C-1}{n_m C}(P/P_0) \quad \text{S1}$$

where: P and P0 are the equilibrium and the saturation pressure of nitrogen at the temperature of adsorption, n is the quantity adsorbed, nm is the monolayer adsorbed gas quantity, and C is the BET constant of the material (Equation S2):

$$C = \exp\left(\frac{E_m - E_L}{RT}\right) \quad \text{S2}$$

where Em is the heat of adsorption for the monolayer, EL is the heat for the second and higher layers and is equal to the heat of liquefaction or heat of vaporisation. S2 is an adsorption isotherm that can be plotted in linear fashion for a restricted portion of the 'BET plot' (0.05<P/P0<0.3):

Finding the intercept and the slope values of the linear 'BET plot', it is possible to calculate the monolayer n_m quantity adsorbed and the BET constant. BET surface is then obtained from the monolayer quantity adsorbed, with the knowledge of the average area occupied by the adsorbate molecules in the complete monolayer σm (also called molecular cross-sectional area), by using Equation S3:

$$A_{BET} = \frac{n_m L \sigma_m}{m} \quad \text{S3}$$

where: σm is the molecular cross-sectional area (0.162 nm2 for N2), L is the Avogadro number, and m is the mass of the sample.

N2 desorption data are recommended for BJH meso-porosity assessment (VBJH and Dav,BJH), as they are representative of a reversible liquid-vapor transition in the case of capillary condensed molecules typical of mesopores. BJH method is an iterative method, it is possible to obtain pore diameter distribution starting

from Kelvin equation. This equation links the pore radius with the relative pressure responsible to the nitrogen adsorption or desorption in the pores (Equation S4):

$$\ln\frac{P}{P_0} = -\frac{2\gamma V_l}{r_k RT} \qquad \text{S4}$$

where γ is the surface tension, Vl is the molar volume, R is the universal gas constant, T is the temperature of the adsorption/desorption measure, rk is the Kelvin radius.

This model is based on two assumptions: (i) all the pores have cylindrical shape, (ii) there are no interconnected pores. Varying the P/P0, the relative adsorbate volume is recorded, obtaining the adsorption isotherm. By the Kelvin equation and BJH method an integral (i.e. cumulative) V=f(d) results. This curve is then differentiated so to get the correspondent diameter distribution curve.

All these calculations are performed by the simple equation 4 VBJH /ABET where VBJH is the BJH desorption pore volume and ABET the BET desorption surface area.

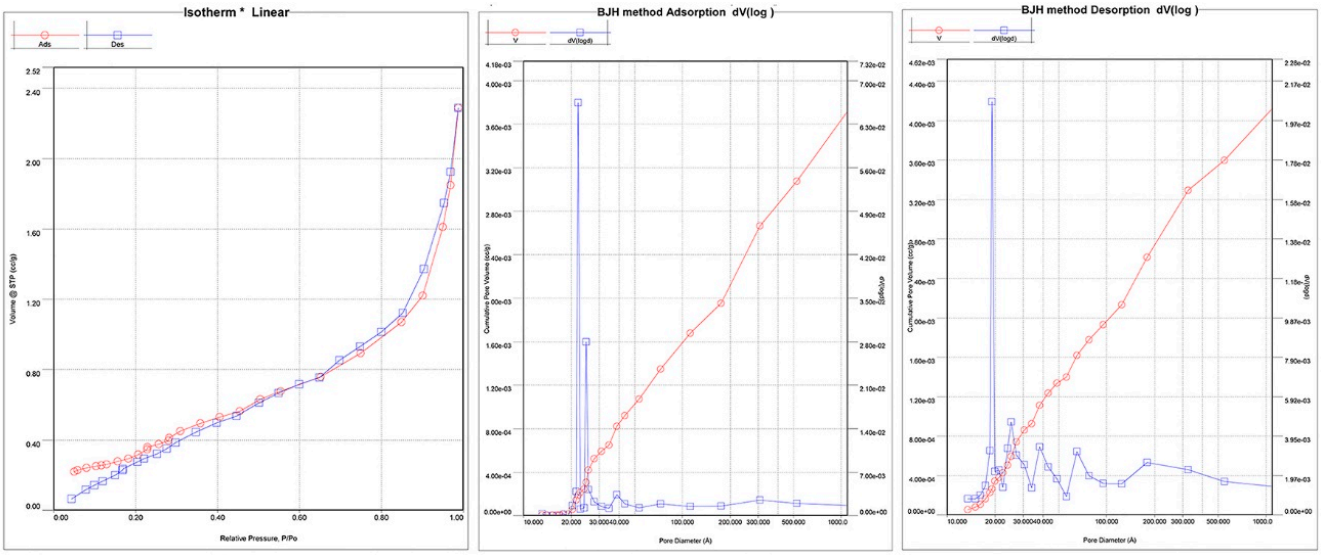

Figure S1. HC_200_0 BET-BJH report analysis

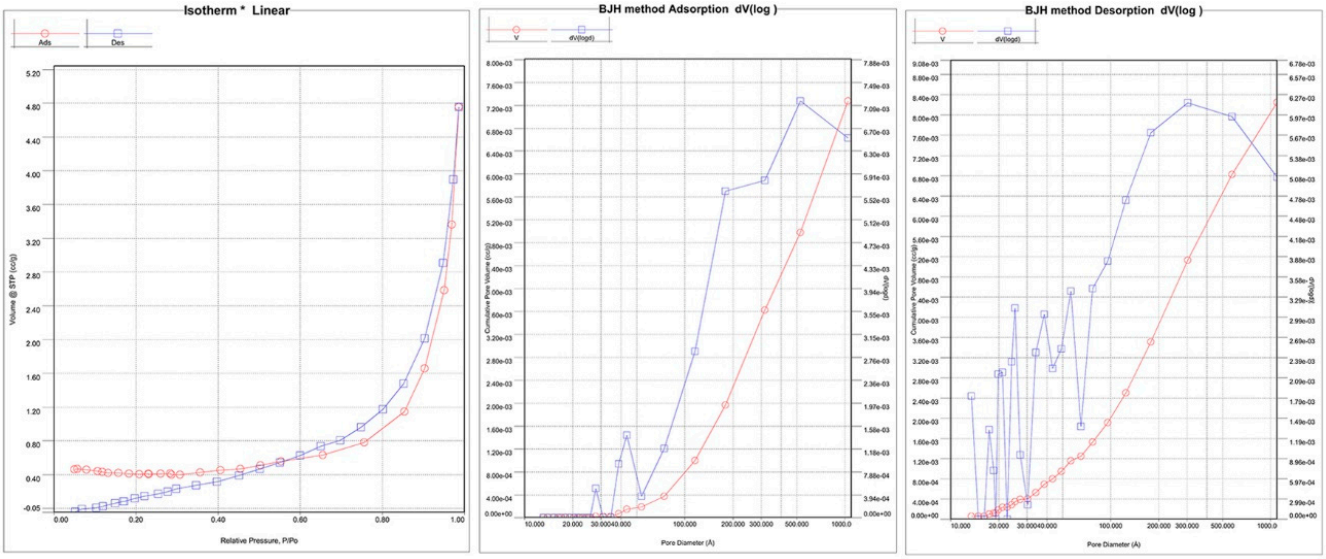

Figure S2: HC_200_120 BET-BJH report analysis

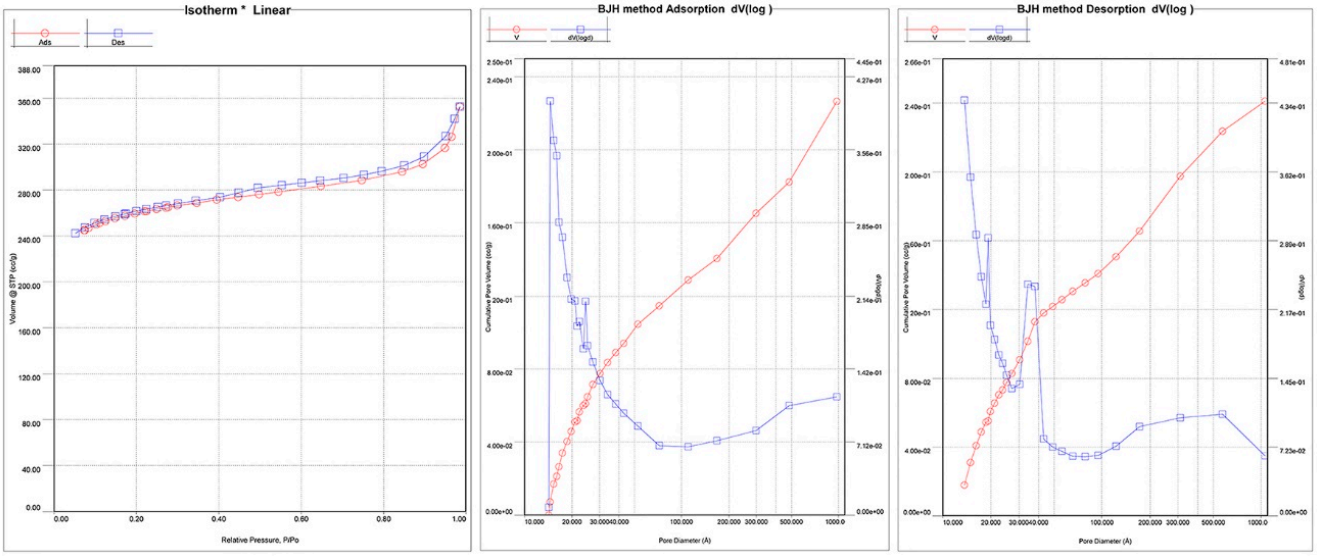

Figure S3: HCA_200_0 BET-BJH report analysis

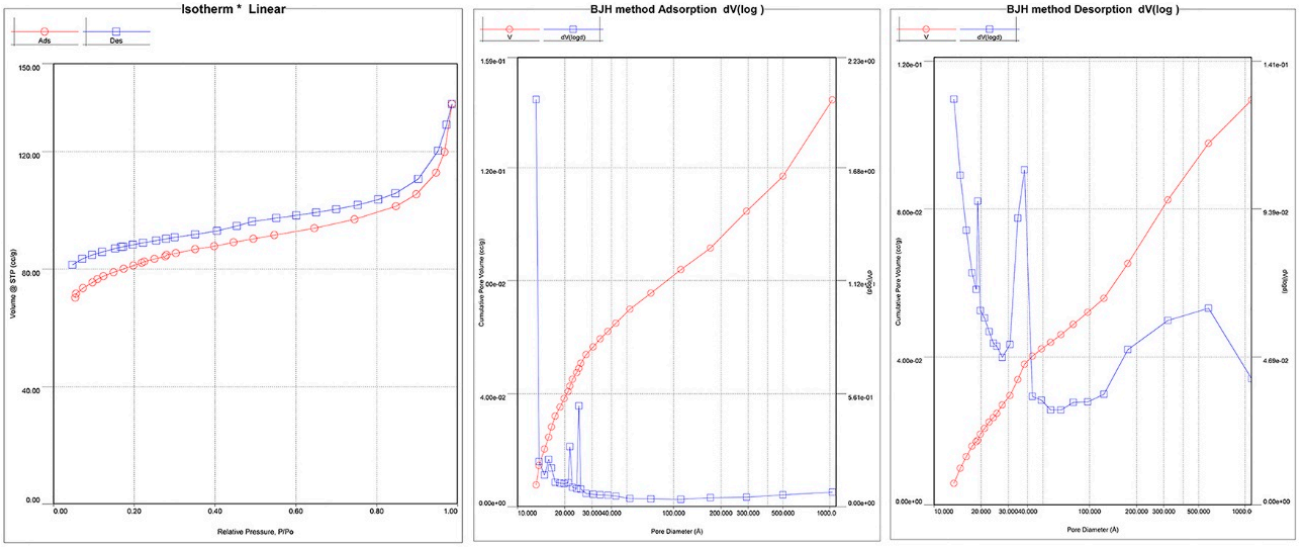

Figure S4: HCA_200_120 BET-BJH report analysis

Elemental and proximate analysis, solid yield, and water characterization

Table S1: Elemental analysis (CHNS) of raw biomass

	C [%dry]	H [%dry]	S [%dry]	O [%dry]
Silver fir	48.46 ± 0.86	6.19 ± 0.09	0.84 ± 0.02	44.32 ± 1.40

Table S2: Solid yield and elemental analysis of hydrochars

Time [min]	Yield	C [%dry]	H [%dry]	S [%dry]	O [%dry]
			Silver fir		
-	-	48.46 ± 0.86	6.19 ± 0.09	0.84 ± 0.02	44.32 ± 1.40
			Hydrochars 200 °C		
0	0.809 ± 0.006	50.29 ± 0.46	6.15 ± 0.09	0.84 ± 0.03	42.73 ± 0.38
120	0.376 ± 0.005	64.92 ± 0.75	5.82 ± 0.08	0.84 ± 0.03	28.42 ± 0.77

Table S3: Characterization of demineralized water

T [°C]	pH	σ [mS/cm]
25.0 ± 0.5	5.857 ± 0.006	0.005

Table S4: Proximate analysis of native biomass, hydrochars, and activated hydrochars (via TGA determination).

Residence time (min)	Ash (%dry)	Fixed carbon (%dry)	Volatile matter (%dry)
		Silver fir	
-	6.91%	5.31%	87.78%
		Hydrochars 200 °C	
0	7.13%	8.16%	84.71%
120	11.81%	14.23%	73.97%