

Application of Experimental Design to Hydrogen Storage: Optimisation of Lignin-Derived Carbons

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Supporting Tables

Table S1: Comparison of BET fitting results to nitrogen isotherms, calculated with the Rouquerol correction applied in the pressure range $p/p_0 = 0.01 - 0.03$. The BET surface area (S_{BET}) uncertainty calculated from the analysis is listed. Repeat isotherms for experiments 1, 5, and 7 indicate a measurement uncertainty of up to $\pm 40 \text{ m}^2 \text{ g}^{-1}$.

Experiment number	S_{BET}	r^2	C
1	$486 \pm < 1$	0.9999987	4795
1 (repeat isotherm)	$501 \pm < 1$	0.9999992	4555
2	432 ± 1	0.9999961	4967
3	537 ± 1	0.9999979	4504
4	$284 \pm < 1$	0.9999977	3587
5	1409 ± 2	0.9999996	579
5 (repeat isotherm)	1412 ± 5	0.9999980	653
5 (repeat sample)	1306 ± 1	0.9999824	733
6	597 ± 1	0.9999977	2308
7	646 ± 1	0.9999984	2936
7 (repeat isotherm)	684 ± 1	0.9999986	1929
8	1055 ± 1	0.9999974	460
9	512 ± 1	0.9999986	3352
10	519 ± 1	0.9999978	3779
11	$502 \pm < 1$	0.9999985	3495

Table S2: Comparison of the magnitude of the power law regime calculated from the Power Law and Gibaud fittings using SasView and Origin respectively. Each experiment number corresponds to synthesis parameters listed in the main document. Values derived from the power law model were used as initial parameters for the Gibaud fitting. The radius of gyration (R_g) derived from the Gibaud model was converted to average pore width (w_{avg} : SAXS) using the relation; $w_{avg} = \left(\frac{5}{3}\right)^{\frac{1}{2}} R_g$.

Experiment Number	n		R_g	w_{avg} : SAXS	χ^2	Adj. r^2
	Power law	Gibaud				
1	3.2	3.3	6.0	7.7	31.6	77
2	3.1	3.2	7.1	9.1	27.4	111
3	3.2	3.3	6.3	8.1	47.2	114
4	3.2	3.3	7.3	9.4	56.3	221
5	2.7	2.8	7.3	9.5	38.9	56
5 (repeat sample)	2.6	2.8	7.2	9.2	15.3	107
6	2.8	2.9	7.1	9.1	47.3	71
7	2.9	3.0	7.7	10.0	55.6	33
8	3.3	3.3	6.6	8.6	49.4	77
9	3.2	3.3	6.8	8.7	31.7	133
10	3.2	3.3	6.5	8.4	36.5	49
11	3.2	3.3	6.0	7.7	31.6	77

Supporting Figures

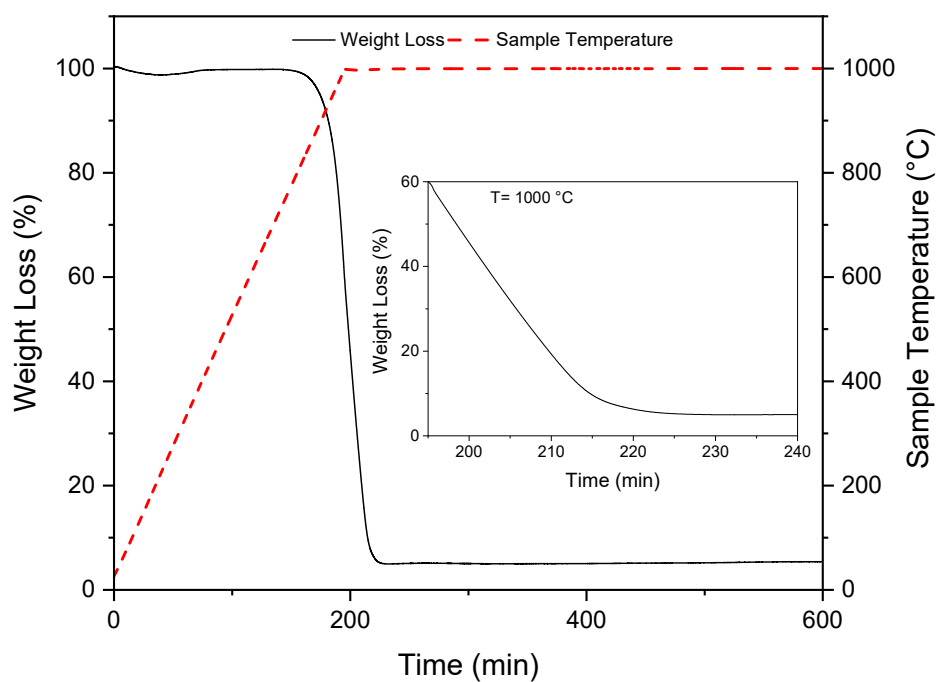


Figure S1: Thermogravimetric analysis was used to approximate the appropriate range for activation dwell time using the most severely treated organosolv lignin char (factors at highest values: carbonised at 900 °C for 360 min). The char was heated in argon at 5 °C min⁻¹ to the highest activation temperature (1000 °C). The gas flow was switched to CO₂ (100 mL min⁻¹) and the weight loss was observed (see inset).

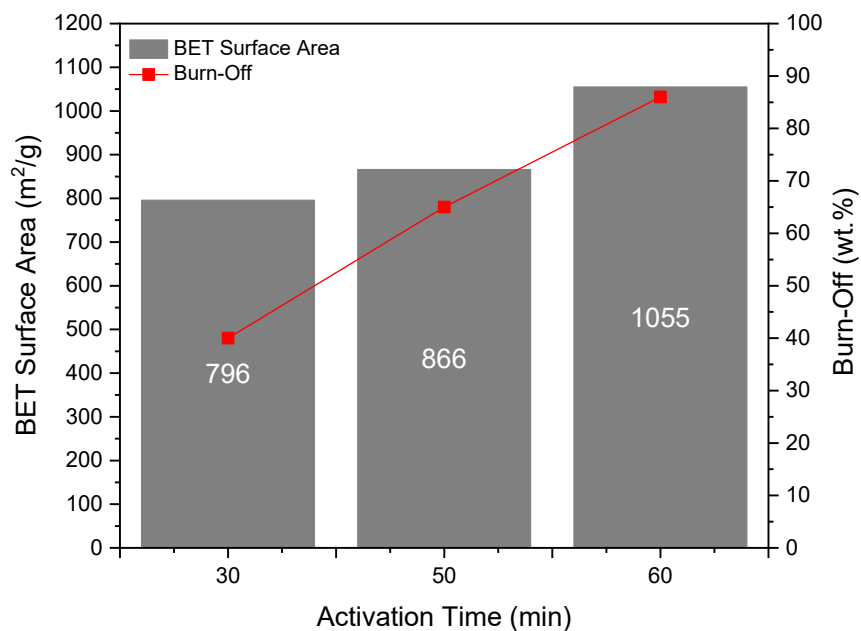


Figure S2: The thermogravimetric analysis experiment (Figure S1) was scaled up to a horizontal tube furnace. Severely treated organosolv lignin chars (carbonised at 900 °C for 360 min) were activated in CO₂ (100 mL min⁻¹) at 1000 °C for 30–60 min. The effect of activation dwell time on the burn-off and BET surface area values of activated carbons was examined.

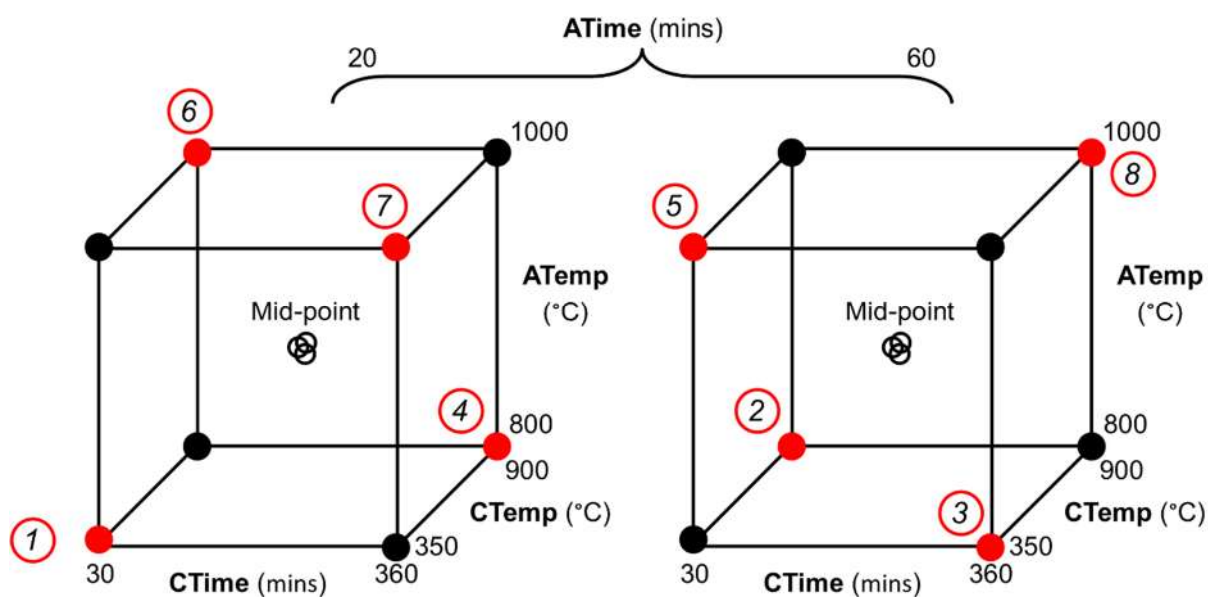


Figure S3: Graphical representation of full factorial experimental design for activated carbon synthesis utilising four factors: activation temperature (*ATemp*), activation dwell time (*ATime*), carbonisation temperature (*CTemp*), carbonisation dwell time (*CTime*). Each corner of the cube represents an experiment (i.e. one activated carbon prepared), factors are varied simultaneously at their highest and lowest levels and three repeats at the mid-point. The experiments performed in a fractional factorial design, where a subset of the experiments is carried out, are highlighted. The experiment numbers (Exp) are listed in the main document in **Table 2**.

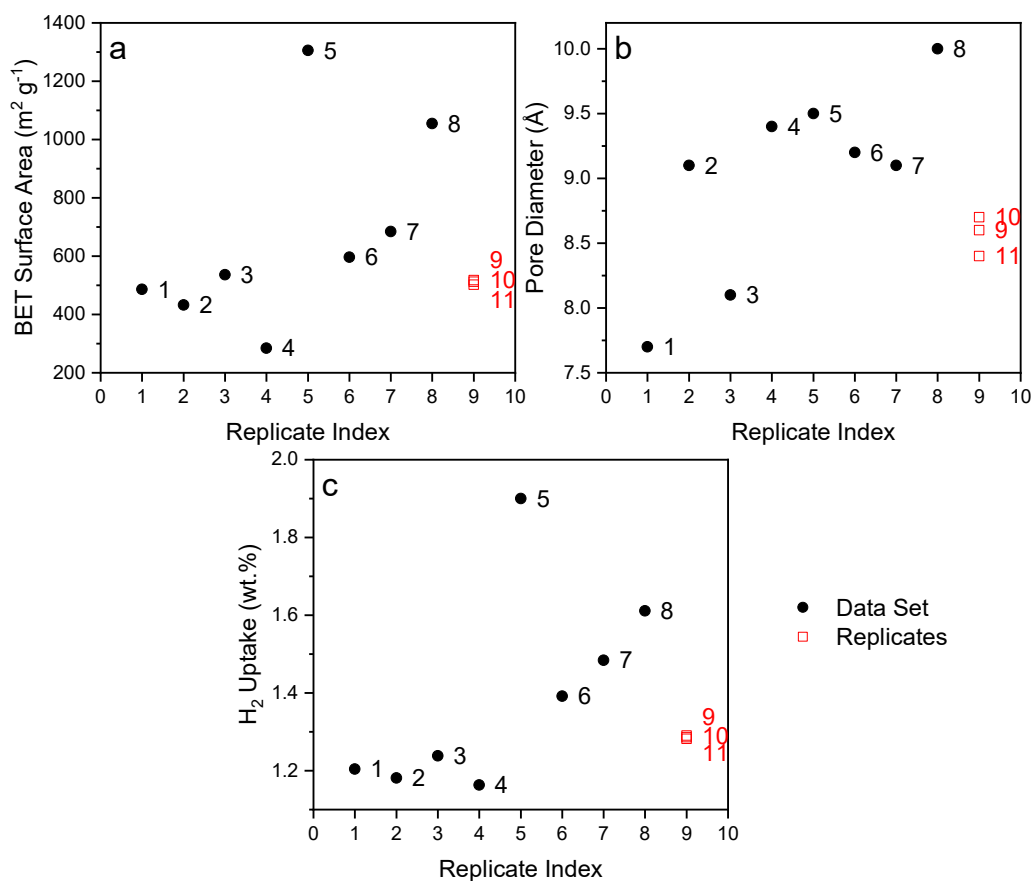


Figure S4: Replicate plots were used to ensure the variation between replicate measurements is smaller than the variation over the data set for each of the measured responses: BET surface area, SAXS-derived average pore diameter, and hydrogen uptake at 77 K. Each point represents a numbered experiment (Exp), with the factors for each listed in the main document in **Table 2**.

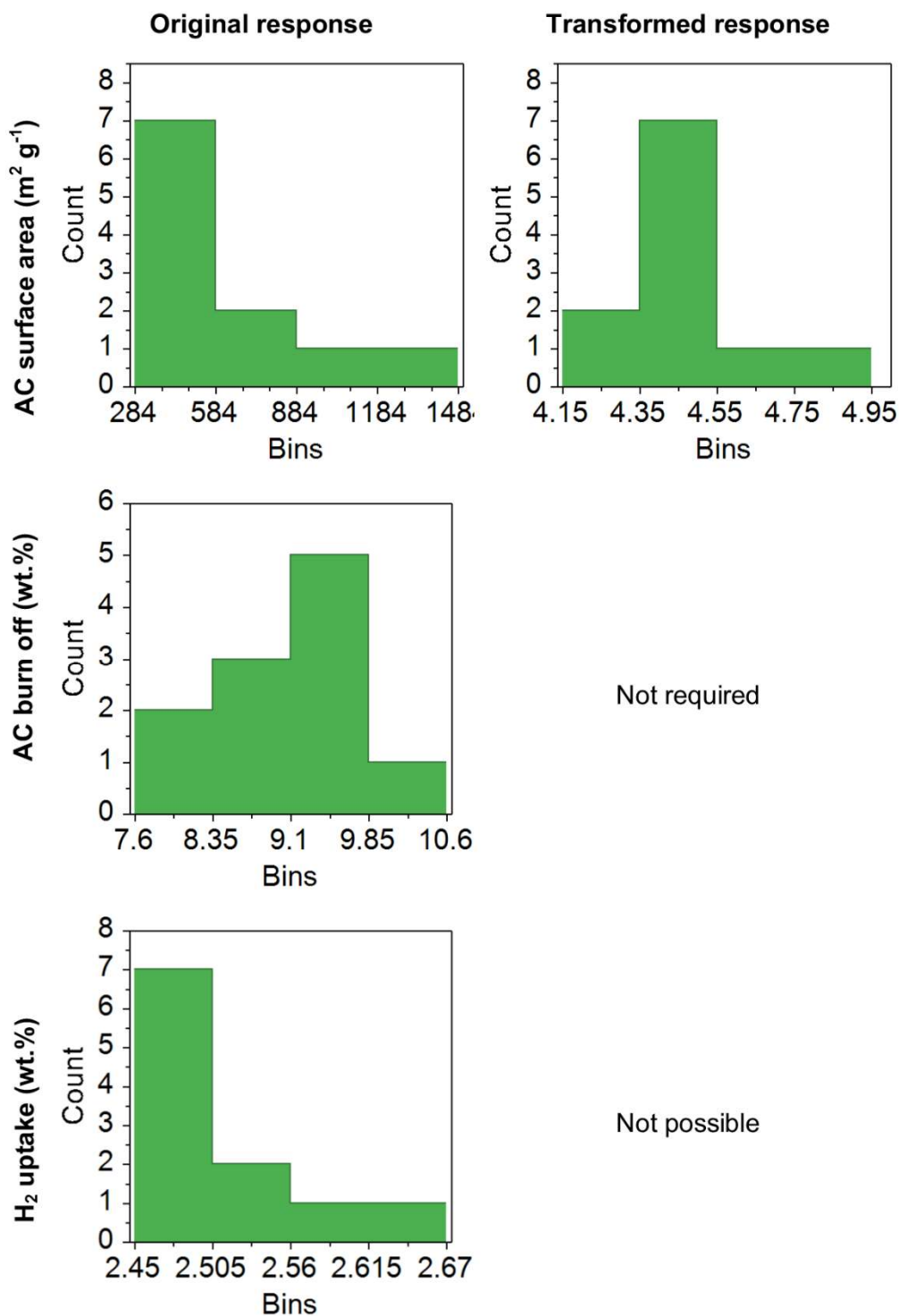


Figure S5: Histograms of response were used to study the distributional shape of the response variables measured for activated carbons (ACs); BET surface area, SAXS-derived average pore diameter, and hydrogen uptake at 77 K. A positive logarithmic transformation was applied to the surface area response to attain a near-normal distribution. Plots were created using MODDE Pro Version 11.0.2.2309.

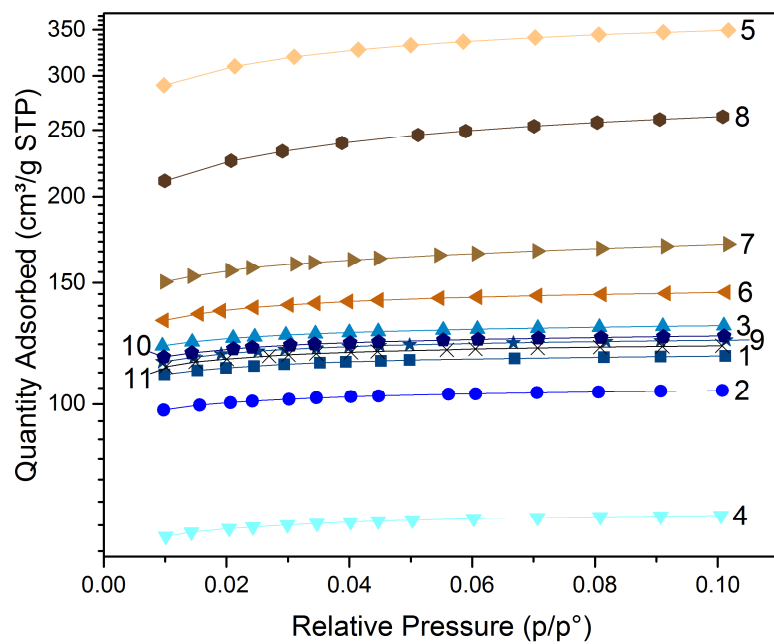


Figure S6: Partial nitrogen isotherms for all experimental design activated carbons recorded at 77 K, labelled by experiment number (**Exp**), with the corresponding synthesis parameters for each listed in **Table 2** in the main document.

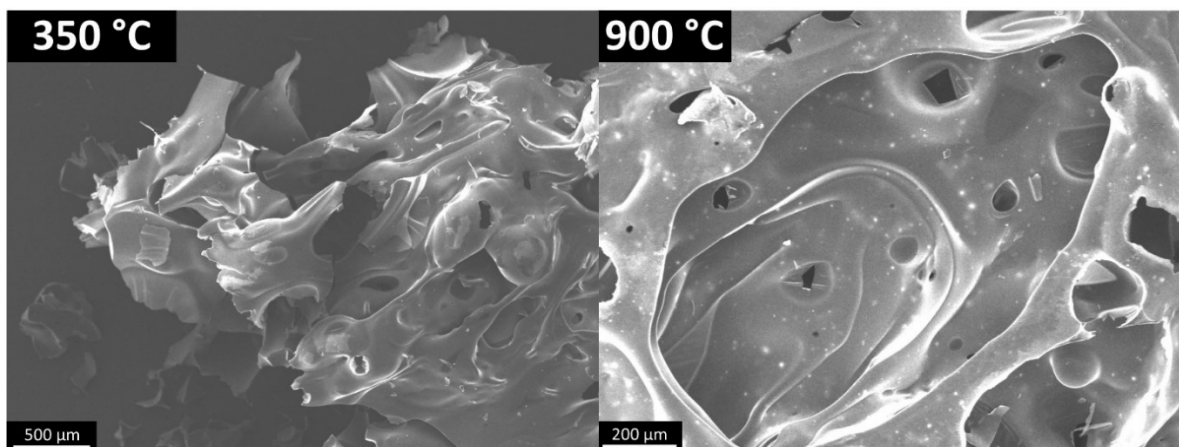


Figure S7: Scanning electron micrographs of lignin-derived chars carbonised at 350 °C and 900 °C for 30 min.

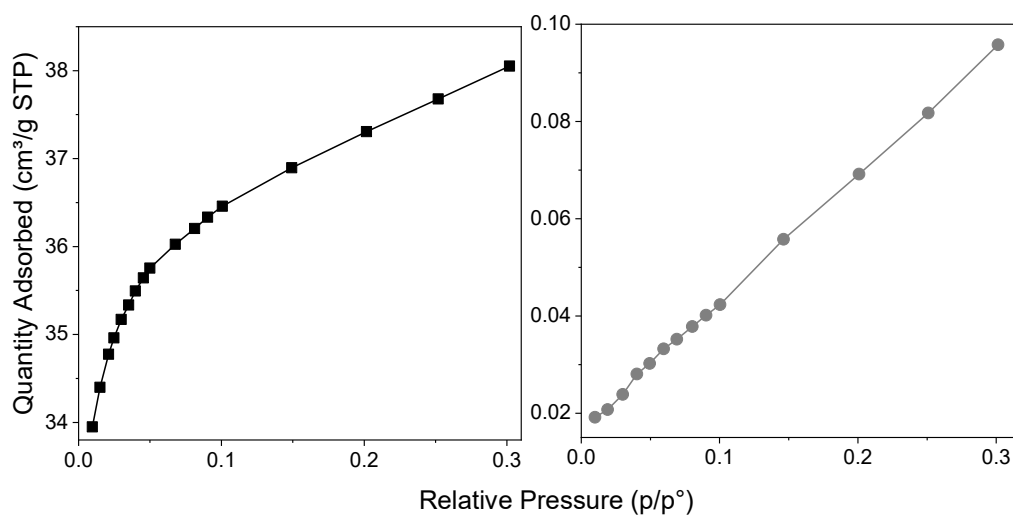
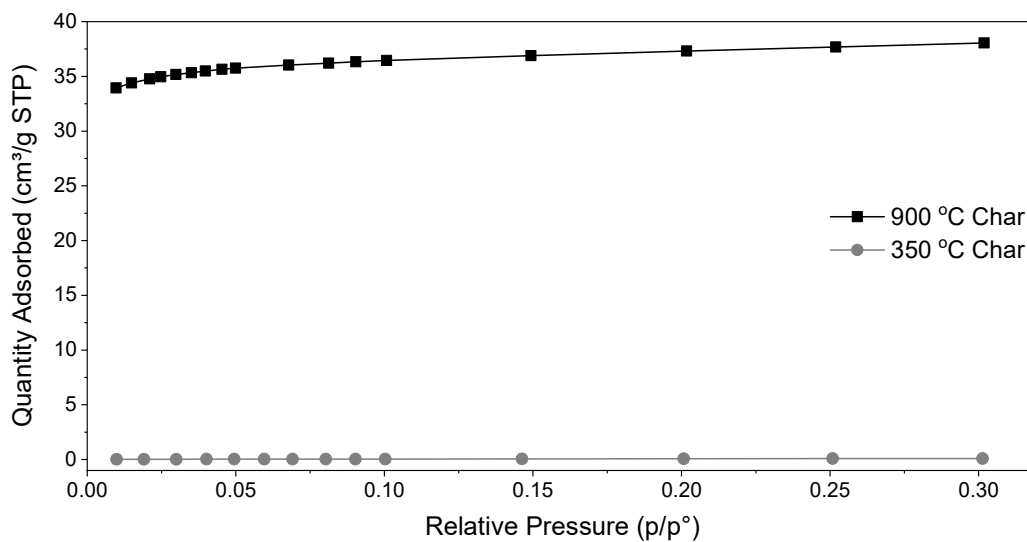


Figure S8: Partial nitrogen sorption isotherms at 77 K for lignin chars carbonised at 350 °C and 900 °C for 30 min.

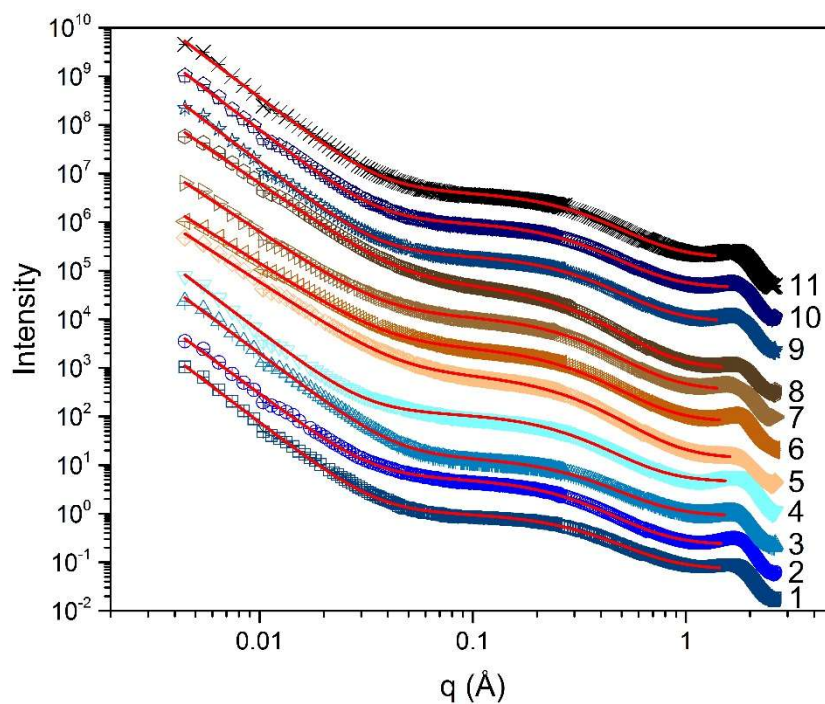


Figure S9: Small angle x-ray scattering (SAXS) profiles of lignin-derived activated carbons. Solid lines represent fitting to the Gibaud model (fitting results listed in **Table S2**), plots are offset along the y-axis for clarity. Patterns are labelled by experiment number (**Exp**), with the corresponding synthesis parameters for each listed in the main document in **Table 2**.

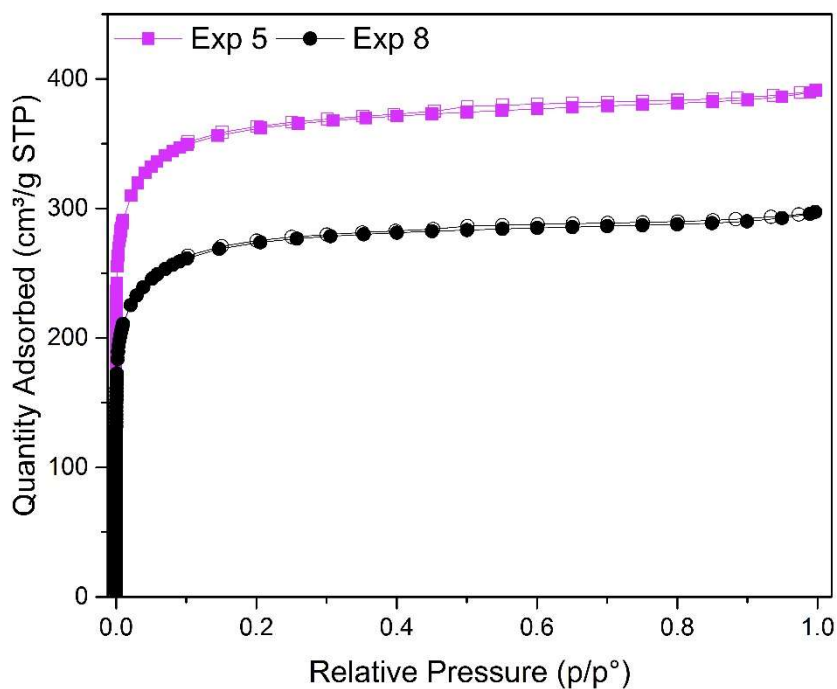


Figure S10: Nitrogen sorption isotherms recorded at 77 K of organosolv lignin-derived activated carbons. The material was carbonised at 350 °C for 30 min (**Exp 5**) or 900 °C for 360 min (**Exp 8**) then activated at 1000 °C for 60 min. The adsorption branch is indicated by filled markers and the desorption branch by hollow markers.