

Introduction

Activated carbons (AC) are disordered, porous carbon materials with many well-known applications in adsorption, purification, gas separation and storage, environmental remediation, and capacitive energy storage. A distinguishing feature of AC materials is that they possess enormous surface areas for adsorption of different substances due to the presence of a large number of nanoscopic pores with entrance dimensions of a few Angstroms up to ~100 nanometers (nm). Micropores, with entrance dimension < 2 nm, are known to act as adsorption sites due to enhanced dispersion forces near micropore walls. Mesopores (2-50 nm) and macropores (> 50 nm) act as pathways to promote transport of adsorptives to the adsorption sites in the microporosity. The NARA Co-Products Team is evaluating the technical and economic aspects of producing AC materials from the insoluble lignin originating from enzymatically hydrolyzed softwood forest residuals. Here we describe the production of AC materials with different porous structures from biorefinery lignin using physical and chemical activation with carbon dioxide (CO₂) and potassium hydroxide (KOH), respectively.

Materials and Methods

- Lignin-rich saccharification residual solids (SRS) were obtained after enzymatic saccharification of SPORL-pretreated softwood forest residuals. Fermentation residual solids (FRS) were slightly different than SRS as they had been subjected to an additional fermentation step.
- Lignin chars were prepared by carbonization in a horizontal tube furnace by heating FRS or SRS at 10°C/min up to a maximum temperature in the range of 700-800°C and holding for one hour under nitrogen (N₂) flow.
- Physical activation consisted of exposing chars to CO₂ at 700°C for varying amounts of time from 5 – 180 minutes and cooling the AC to room temperature under N₂.
- Chemical activation was accomplished by mixing SRS with an aqueous solution of KOH (50 wt%) and evaporation of water at 105°C prior to carbonization. Mixtures with 3 different KOH:SRS ratios (2, 3, and 4) were heated to different temperatures (700, 750, or 800°C) under N₂ and held for one hour. After cooling under N₂ the samples were washed with water and dilute HCl to remove the activation agent.
- Gas physisorption with N₂ and CO₂ was used to obtain adsorption isotherms from which information regarding the AC pore volume, surface area, and pore size distribution was obtained.

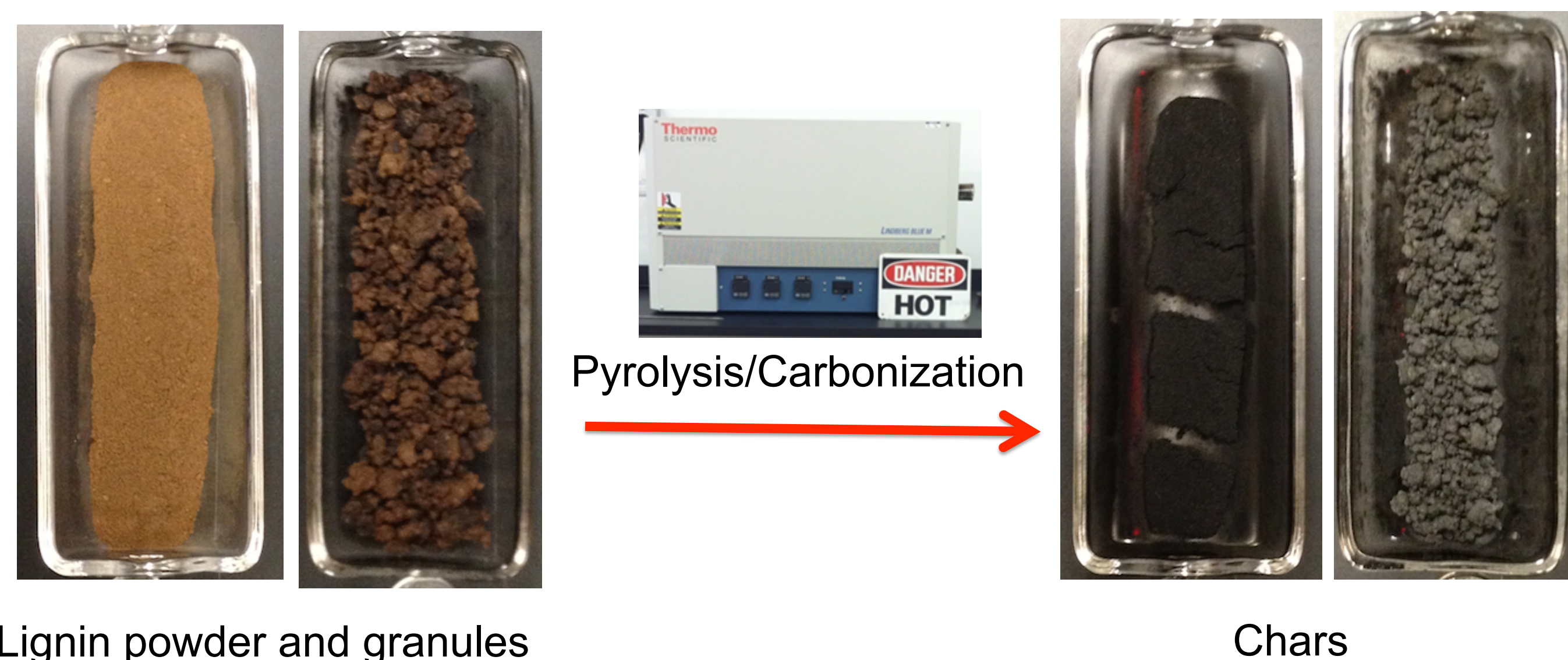


Figure 1: Photographs showing lignin powder and granules before and after carbonization.

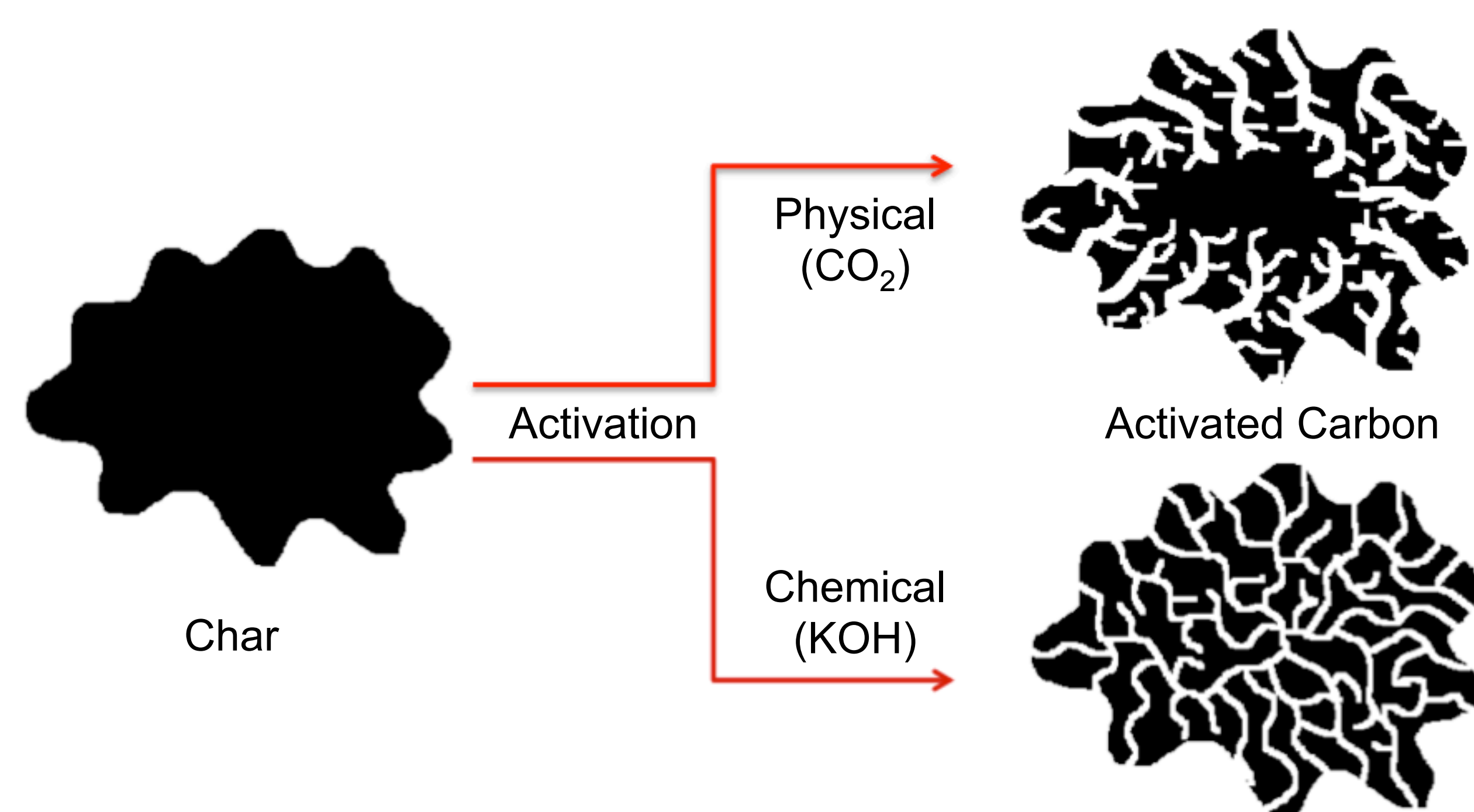


Figure 2: Schematic representation of porosity development during physical and chemical activation.

SEM and TEM imaging of AC

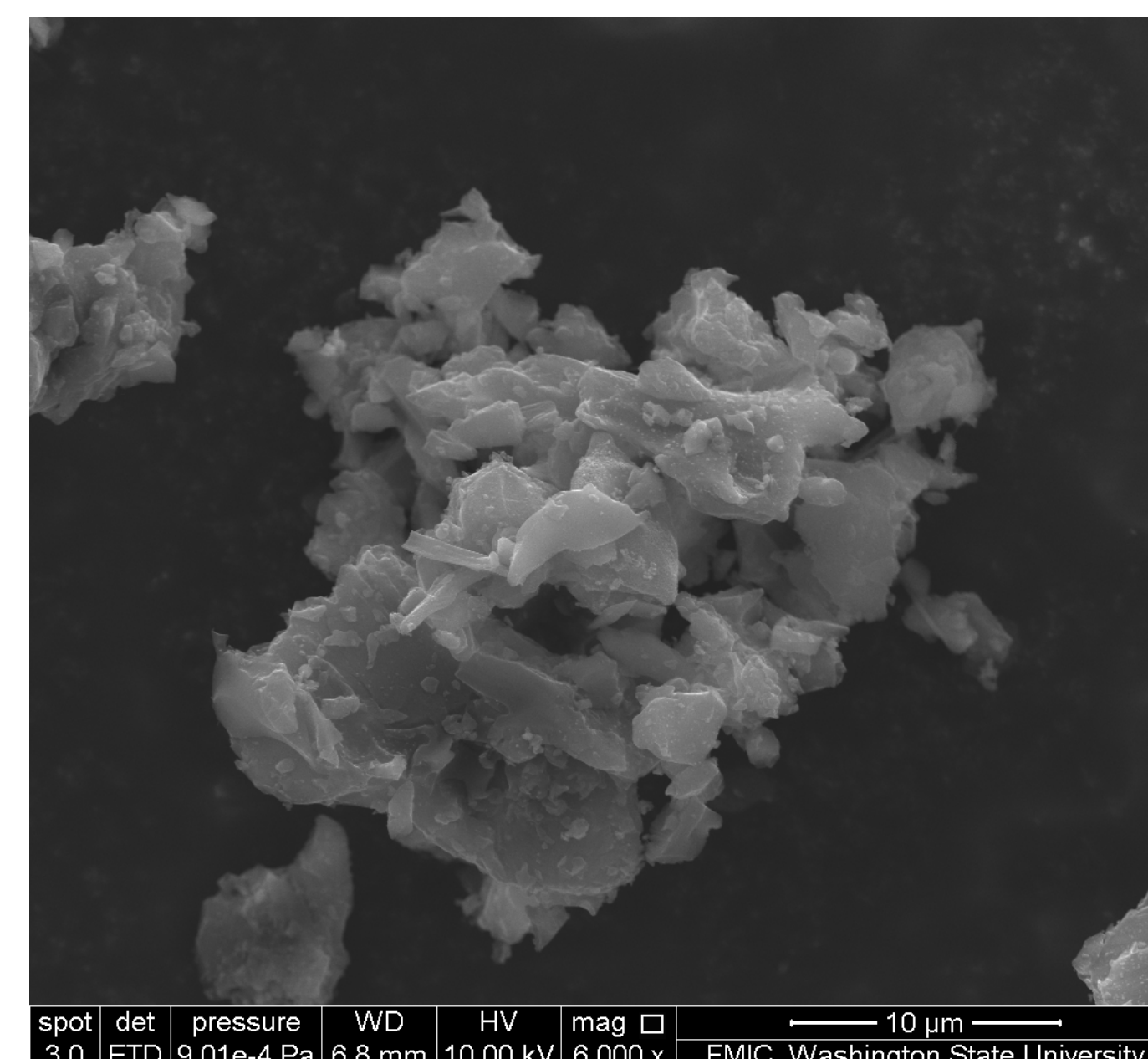


Figure 3: SEM image of AC prepared with CO₂ activation. Scale bar = 10 μm

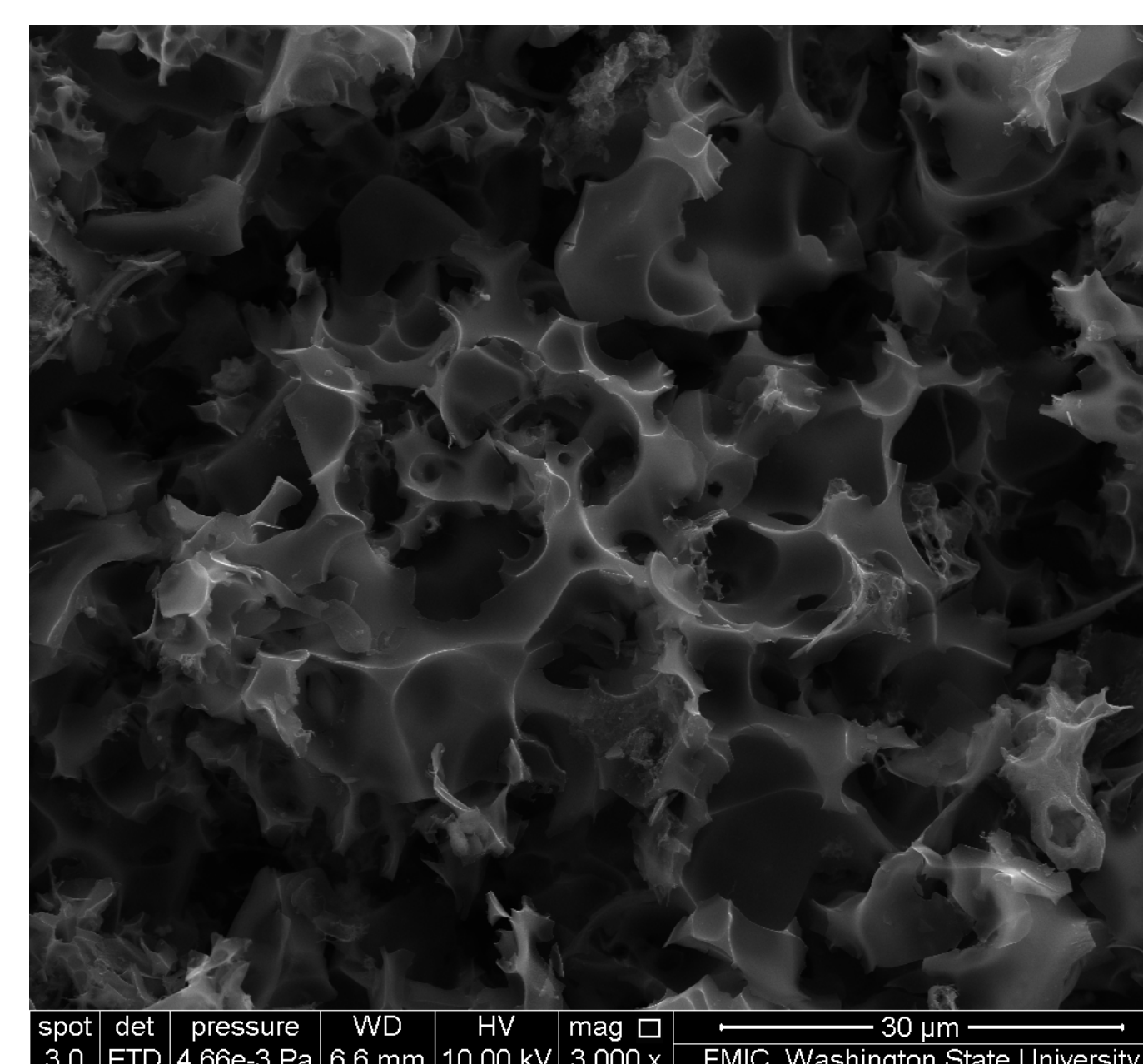


Figure 4: SEM image of AC prepared with KOH activation. Scale bar = 30 μm

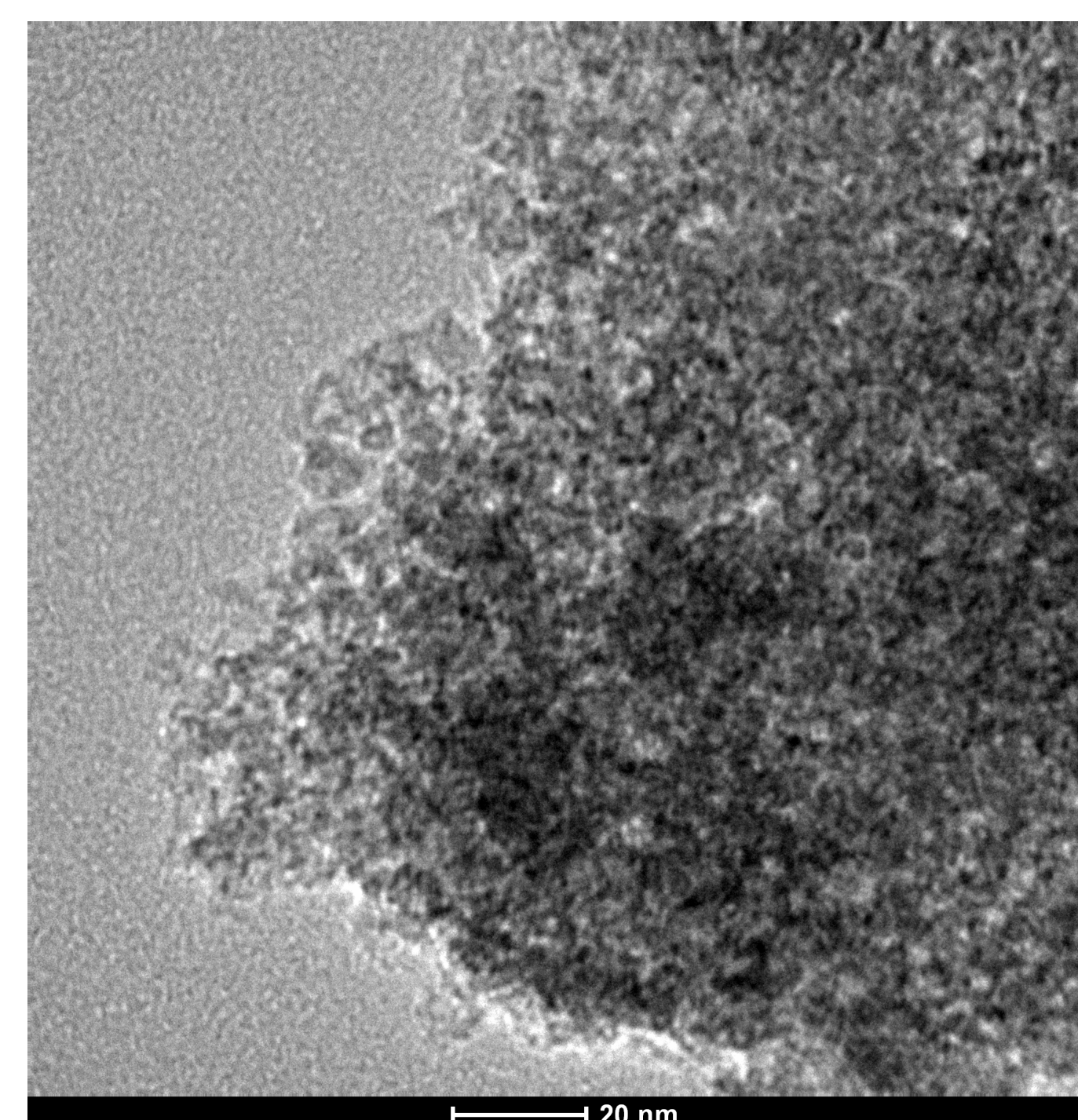


Figure 5: TEM image of AC prepared with CO₂ activation. Scale bar = 20 nm

Adsorption Isotherms

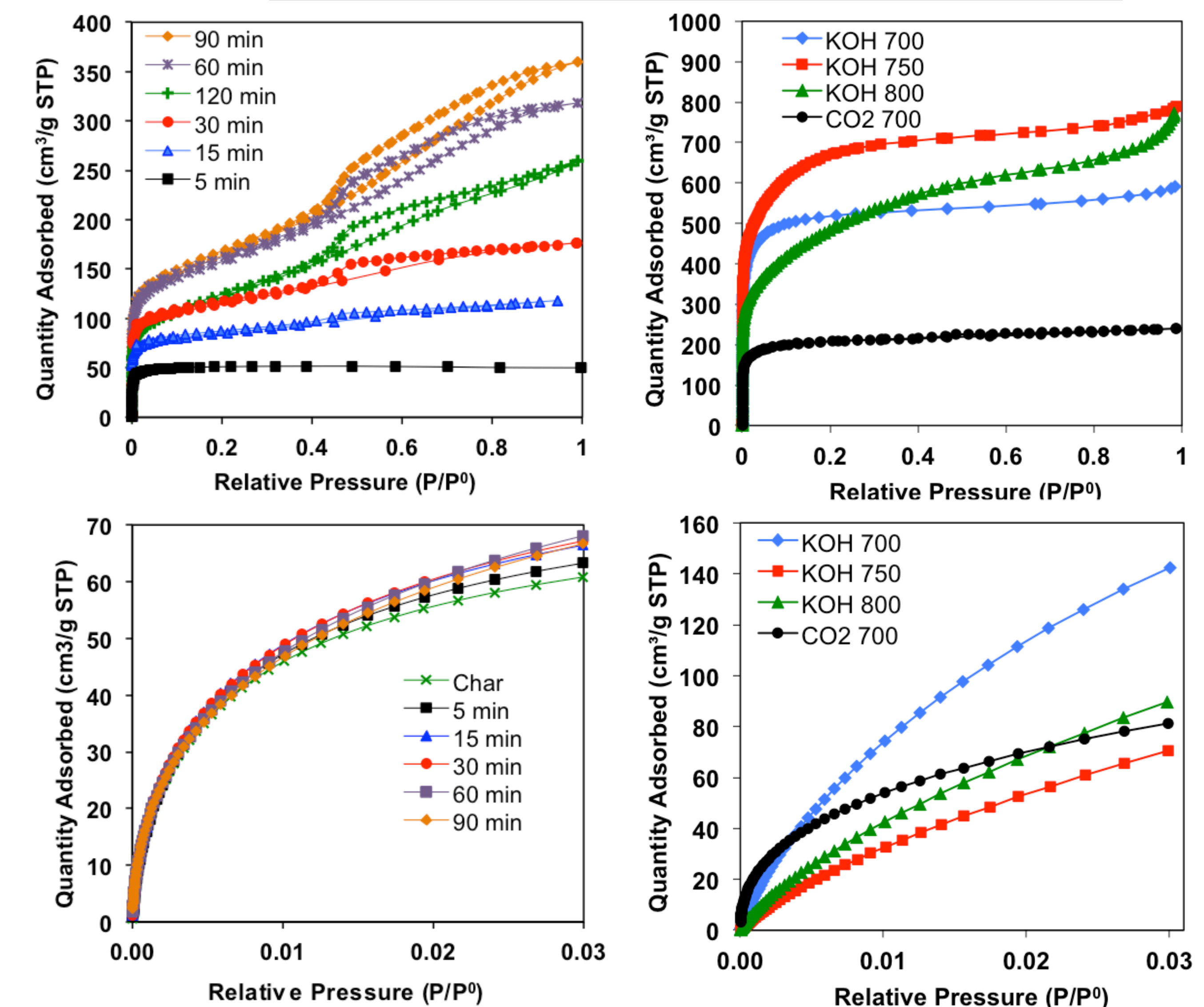


Figure 6: N₂ (top) and CO₂ (bottom) adsorption isotherms of FRS-based AC prepared by CO₂ activation for different times.

Figure 7: N₂ (top) and CO₂ (bottom) adsorption isotherms of SRS-based AC prepared by CO₂ activation (180 min) or KOH activation (KOH:SRS = 3)

Pore Size Distribution by NLDFT

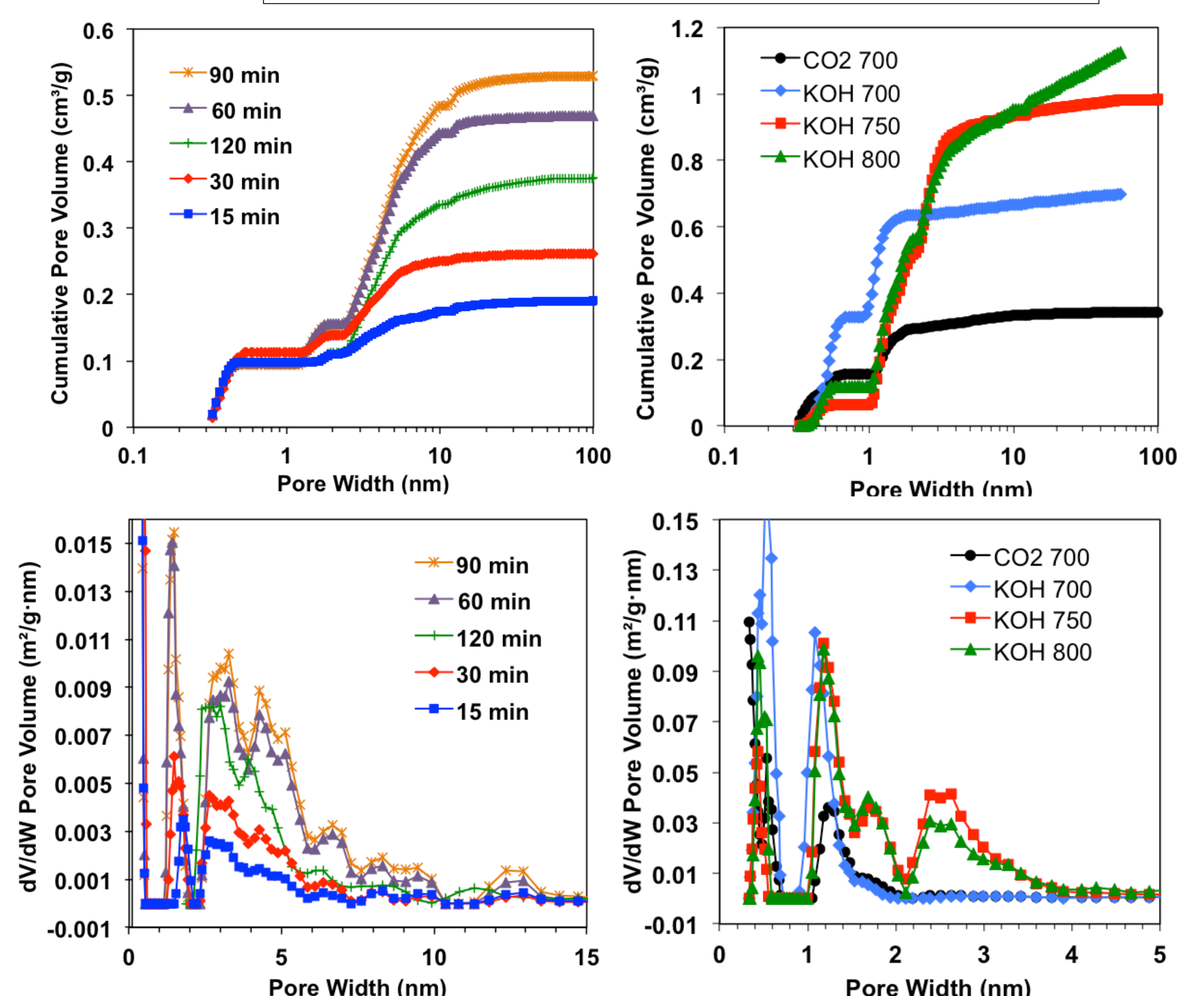


Figure 8: Cumulative (top) and differential (bottom) pore size distributions of FRS-based AC prepared by CO₂ activation calculated with NLDFT (nonlocal density functional theory)

Figure 9: Cumulative (top) and differential (bottom) pore size distributions of SRS-based AC prepared by CO₂ activation (180 min) or KOH activation (KOH:SRS = 3) (NLDFT)

Summary of Porosity Data

Type of Lignin (FRS or SRS)	Activation Agent	Max. Temp. (°C)	Activation Time (min)	KOH: Lignin ratio (w/w)	Total Pore Volume (cm ³ /g)	Mesopore/ Micropore Ratio (v/v)	Apparent BET surface area (m ² /g)
FRS	none	700	0	0	0.03	0	87
FRS	CO ₂	700	5	0	0.08	0	220
FRS	CO ₂	700	15	0	0.20	0.54	366
FRS	CO ₂	700	30	0	0.28	0.93	433
FRS	CO ₂	700	60	0	0.49	1.94	556
FRS	CO ₂	700	90	0	0.55	2.53	563
FRS	CO ₂	700	120	0	0.39	2.36	425
SRS	CO ₂	700	180	0	0.37	0.17	791
SRS	KOH	700	60	2	0.78	0.11	1719
SRS	KOH	700	60	3	0.92	0.11	1989
SRS	KOH	700	60	4	0.74	0.06	1705
SRS	KOH	750	60	2	1.13	0.23	2236
SRS	KOH	750	60	3	1.22	0.22	2405
SRS	KOH	750	60	4	1.41	0.51	2487
SRS	KOH	800	60	3	1.20	0.93	1691

Conclusion

- Physical activation of FRS char with CO₂ produced AC materials with a high proportion of mesoporosity and larger pore sizes compared to chemical activation with KOH.
- Chemical activation of SRS with KOH can produce AC with high micropore volumes and apparent internal surface areas compared to physical activation with CO₂ but the pore size is mainly in the micropore (< 2 nm) and small mesopore (~2-4 nm) range.
- Narrower micropore size distribution centered at smaller average pore sizes was observed at lower activation temperature during chemical activation.
- Differences in lignin pretreatment and isolation procedure affect the reactivity and porosity development during physical activation. This point requires further study in future work.