

Impact of Production Pathway on Nanoporosity of Carbonaceous Sorbents for CO₂ Adsorption

Mikhail Gorbounov¹, Emilie Diaz-Vasseur¹, Rafał Panek² and Salman Masoudi Soltani¹

¹Department of Chemical Engineering, Brunel University London, Uxbridge UB8 3PH, United Kingdom

²Department of Construction Materials Engineering and Geoengineering, Lublin University of Technology, Lublin, 20-618, Poland

Abstract — Climate change requires immediate action from humanity with Carbon Capture and Storage (CCS) standing out as one of the prominent mitigation techniques. Adsorption CCS using carbonaceous nanoporous sorbents has been shown to be a promising route for industrial decarbonization. Such sorbents are often derived from organic waste, with the production pathway consisting of different steps, namely, carbonization, pelletization (with various binders) and activation. The latter two steps, however, could vary in their order, i.e. *activation of the pellet versus the pelletization of the activated powder*. Herein, both of these approaches have been conducted and the impact of the production pathway (as well as the presence of the binder itself) on the nano-structure of the material has been examined and compared to the “baseline-case” of the non-activated carbon (both powder and pellet). The samples were analyzed *via* Proximate Analysis, Fourier-Transform Infrared Spectroscopy and Scanning Electron Microscopy. CO₂ adsorption was evaluated *via* Thermogravimetric Analysis (TGA). Further, the mechanical properties of the nanoporous pellets were studied.

I. INTRODUCTION

One of the main challenges currently facing humanity is the climate crisis. Within this, the abatement of CO₂ emissions from the power sector is an essential step towards decarbonization around the globe requiring immediate action. A proposed solution is Carbon Capture and Storage (CCS): a preventative measure, which centres on immobilizing the carbon dioxide molecule before it is released into the atmosphere. Furthermore, if this approach is applied to a biomass-fired power plant, this process becomes net-negative. This is due to the fact that the CO₂ absorbed by the plant during its growth is not released into the atmosphere (upon combustion of this fuel type) as it is instead, captured (e.g. using solid adsorbents and/or liquid solvents). The combined technology – referred to as Bioenergy with Carbon Capture and Storage (BECCS) – is attracting ever-growing attention and recognition by both the scientific community and policy-makers worldwide. For instance, the Intergovernmental Panel on Climate Change (IPCC) has long suggested BECCS to play a crucial role in limiting global warming to the 2 °C target [1], whilst the UK government expects BECCS as “green” power source to help deliver negative emissions, significantly contributing to

the ambition of removing five million tonnes of CO₂ per year by 2030 [2]. Nevertheless, this technology is not without its challenges. Upon combustion of the sustainable biomass feedstock, vast amounts of co-generated ash are produced (mean yield of just under 7% [3]). Annually, within the UK context, ~52 kilotonnes of (exclusively) wood ash are generated [4]. Since biomass ash cannot be deployed for the same secondary applications as coal ash, most of it ends up being landfilled constituting an environmental hazard. Consequently, valorization of this waste as a precursor for the synthesis of nanoporous adsorbents for CO₂ capture could help alleviate the burden of ash management, whilst simultaneously providing the grounds for cost-effective *in-situ* decarbonization of the biomass firing power plants. Our previous works have served as the *proof of concept*, successfully demonstrating the feasibility of extraction of carbonaceous nanoporous sorbents [5] followed by development of pronounced porosity [6]. However, industrial deployment requires a significant increase in the size of the adsorbent (i.e. from μm-scale (fine) powder, to mm-scale particles) whilst preserving the porous structure and more importantly, meeting the required mechanical stability. This would facilitate a higher heat transfer rate in the adsorption column [7] and ease of handling [8].

Classically with carbonaceous sorbents derived from waste (often bio-residues) [9], the organic precursor has to be first carbonized to shift away from the fibrous network towards a char, which is then activated to produce a prominent porous structure. Often, one of these steps is presupposed by grinding of the material, resulting in powder activated carbon (AC). Additionally, in the cases of chemical activation, the material has to undergo a washing step to relieve the surface of any remaining activating agent. This final process stands in the way of pre-binding organic precursors as it could result in destruction of the produced particle [10]. As such, the production pathway is *activate-then-pelletize*. For instance, carbonaceous adsorbents from hazelnut shells [10] or from waste from the textile industry [8] have followed this procedure from grinding of the raw organic precursor to binding the AC powder into various shapes and sizes. Furthermore, commercial ACs have been

mixed with polyvinyl alcohol (PVA) [7], ionic liquids [11], as well as other organic and inorganic binders [12].

Nevertheless, carbonization and activation of pre-formed materials has also been investigated, e.g. in the context of coal- [13][14] or sewage sludge-based ACs [15]. Further, the “*pelletize-then-activate*” approach has been studied for such precursors as rice straw, olive stones, different nut shells and other biomass wastes, although, the production pathway was somewhat different [16]. The raw materials were first carbonized, followed by milling of the char. Afterwards, the produced powder was formed into pellets and only then physically activated. Due to this approach, the authors have noticed the passing of the organic binder into the gas-phase upon high temperature activation [16]. Similar pathways have also been undertaken for AC briquettes from eucalyptus wood [17].

To the best of our knowledge, there is little research into the influence of the order of the procedure onto the nano-structure of the produced sorbents, the CO₂ adsorption capacity as well as the variation in mechanical strength. As such, herein, we are building upon our previous works [5] [6] in order to facilitate industrial applicability of biomass combustion bottom ash-derived carbonaceous adsorbents.

II. MATERIALS AND METHODOLOGY

Industrial-grade bottom ash was sourced from Drax power plant - the largest biomass-fired power plant in the UK - located in Selby, England. The procedure for deriving the virgin (i.e. not activated) carbon was described in our previous work [5], whereas the activation of the samples (powders and pellets) followed a pathway described in [6].

The organic binder was produced from PVA (CAS 9002-89-5; Mw = 85,000 – 146,000) which was obtained from Sigma-Aldrich. The polymer was dispersed in deionized water (5% wt. of PVA to 95% wt. of H₂O) and was left under continuous stirring (400 rpm) overnight under a reflux at a constant temperature of 90 °C. The resulting viscous liquid binder was then used in the process of pelletization.

In order to produce pellets, the carbon powder (virgin or activated) was first mixed with the prepared 5% PVA binder solution. When using an organic binder, reasonable mechanical properties can only be achieved if a high amount of binder is added [12]. As such, a ratio of carbon to binder of 1:1.5 was employed. If needed, additional deionized water was added to produce an extrudable paste. The resulting substance was then manually extruded through a syringe onto a Petri dish and placed into an oven (60 °C) to dry overnight. Following this pathway, the virgin carbon pellet (VCP) and the activated-then-pelletized (A-P) samples were produced. The pelletized-then-activated (P-A) sample was obtained by activating the VCP pellets as per [6].

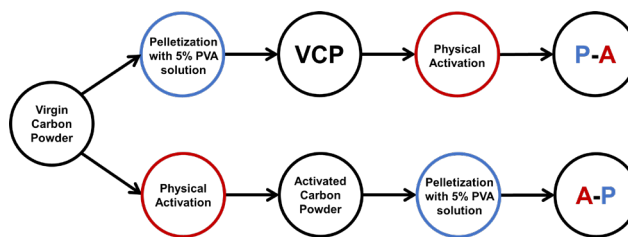


Figure 1. Schematic of evaluated adsorbent production pathways.

The adsorption capacity of the nanoporous materials was evaluated *via* TGA (Mettler Toledo TGA 2), the surface morphology was examined on a Scanning Electron Microscope (LEO 1455VP), the surface functional groups were studied using a Fourier-Transform Infrared Spectroscopy (Shimadzu IRSpirit), whereas Proximate Analysis was conducted as per ASTM D3172 [18]. The nanoporosity was examined employing the standard BET method [19], i.e. N₂ adsorption/desorption at 77 K, on a sorption analyzer (Micromeritics ASAP 2020). The pellets were purged (degassed) for 6 hours at 200 °C (ramp rate = 15 °C/min) prior to the experiment. The mechanical properties were studied using a crush-strength tester (Mecmesin MultiTest-dV) following the methodology described in ASTM D6175 [20] (although, the drying of the samples was performed at 60 °C in order to avoid subjecting the samples to a significant thermal treatment).

III. RESULTS AND DISCUSSIONS

A. Scanning Electron Microscopy (SEM)

The VCP, P-A and A-P pellets were examined under an electron microscope (Figures 2 – 4).

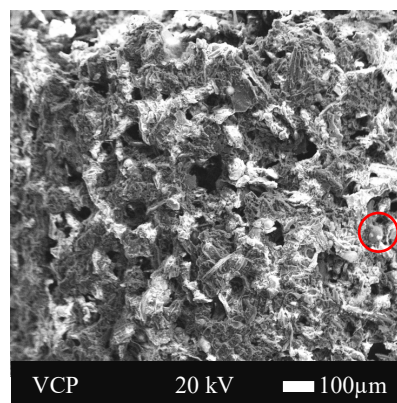


Figure 2. The virgin carbon pelletized (VCP) adsorbent.

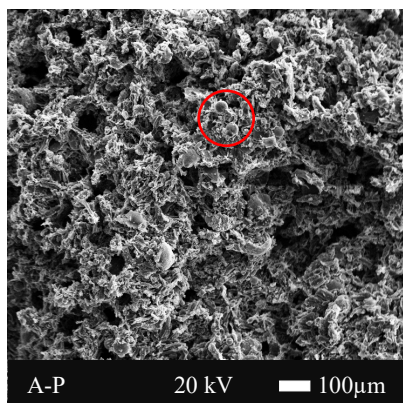


Figure 3. The *activated-then-pelletized* (A-P) adsorbent.

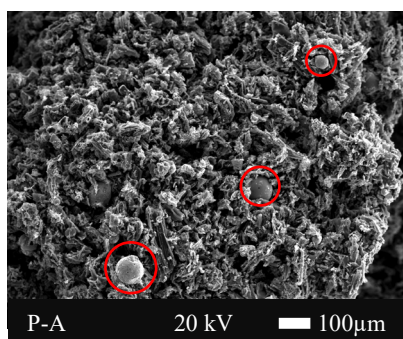


Figure 4. The *pelletized-then-activated* (P-A) adsorbent.

As seen in the figures, pelletization has resulted in the creation of large macropores, especially in the VCP and the A-P samples. Further, the spherical ash impurities (i.e. aluminosilicates from the raw ash) have also been clearly incorporated into the pellet (highlighted with red circles).

B. Proximate Analysis

Proximate Analysis results allow to calculate the quantity of ash impurities alongside the fixed carbon, the volatile organic compounds (VOC) and moisture contents in the sample. The obtained data for the three samples studied in this work is shown in Table I.

TABLE I. PROXIMATE ANALYSIS RESULTS.

Sample Name	Moisture, wt%	VOC, wt%	Fixed C, wt%	Ash, wt%
VCP	2	40.5	36	21.5
P-A	1	8.5	57.5	33
A-P	1	14.5	53.5	31

The increased ash and fixed carbon content of the activated sample is associated with the loss of VOCs due to activation. Further, Table I corroborates the hypothesis of PVA decomposition upon activation (potentially propagating lesser mechanical stability of the P-A samples). Regardless, the higher VOC content of the pellets compared to their powder-form analogues [6] indicates presence of PVA within the materials.

C. Surface Area and Porosity Analysis

The order in which the pelletization and activation steps are done, affects the development of nanoporosity as can be visualised from Table II.

TABLE II. SURFACE AREA AND POROSITY ANALYSIS.

Sample Name	S_{BET} , m^2/g	Total pore V, cm^3/g	Average pore size, nm
VCP	4.0	0.0066	4.5
P-A	334	0.0778	3.5
A-P	120.2	0.0194	3.3

Firstly, activation improves the porous structure of the pellets, leading to a considerable enhancement of both pore volume and surface area. In addition, such thermal treatment mostly produces micropores and/or small mesopores on the surface of sample (as can be evidenced by the reduced average pore size), a desirable characteristic in CO_2 adsorption (i.e. favourable adsorption sites).

Herein, however, there are major disparities between the activated samples. The lesser porosity of the A-P framework indicates the potential blocking of available adsorption sites by PVA-based binder. In turn, the significantly higher pore volume and S_{BET} of the P-A pellet may further imply (partial) loss of binder upon activation, suggesting potentially compromised mechanical stability.

D. Fourier-Transform Infrared Spectroscopy (FTIR)

Infrared spectra of the carbon pellets were retrieved using the Attenuated Total Reflection (ATR) methodology in the region of $600 - 4000 \text{ cm}^{-1}$ at a step size of 4 cm^{-1} . The infrared spectra of the evaluated pellets are presented in Figure 5.

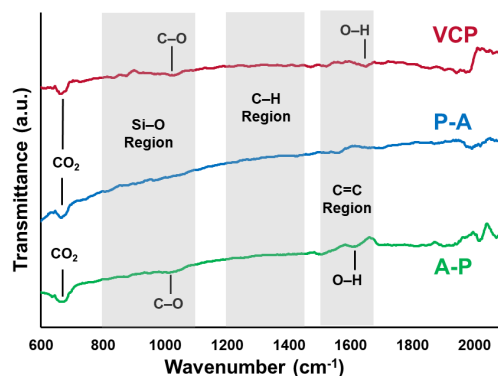


Figure 5. Infrared spectra of the investigated materials: VCP (top; red), P-A (middle; blue) and A-P (bottom; green).

Since the materials have similar origins, it is expected of them to “share” peaks. For instance, the minor peaks between $\sim 800 \text{ cm}^{-1}$ and $\sim 1100 \text{ cm}^{-1}$ are commonly found across all of the samples. They could be ascribed to various ash impurities (i.e. different Si-O bonds and their vibrations) [21]–[23]. Within that, however, the VCP and A-P samples present peaks that could also be identified as different C-O modes, namely, stretching vibrations at wavenumbers between 1030 and 1050 cm^{-1} [24]. A further commonality can be distinguished at $\sim 669 \text{ cm}^{-1}$ as it might represent the

CO₂ from the background [25]. The plethora of minor peaks in the region of approximately 1200 cm⁻¹ and 1400 cm⁻¹ represent the different C-H vibrations [22]. Further prominent peaks can be identified in the region, where the stretching vibrations of the C=C bonds are believed to lie [26]–[28], proving the carbonaceous nature of the pellets. However, the bands present on the VCP and P-A spectra around the wavenumber of 1630 cm⁻¹ could be alternatively assigned to the hydroxyl functional group.

As evident from Figure 5, activation has eliminated the surface functionalities from P-A sample. As such, the lack of hydroxyl or C-O group peaks on this sample corroborates loss of the PVA-based binder upon activation, a clear indication of the effects of the production pathway. This may suggest a potentially lower resistance to crushing due to (partial) decomposition of the binder. On the other hand, both VCP and A-P spectra contain the PVA-associated bonds, proving incorporation of the binder into the framework of the pellet.

Nevertheless, the evaluated spectra did not produce prominent peaks for the hydroxyl groups (to be expected in the region 3300 – 3400 cm⁻¹ [24]), hence, the spectra have been cut off at 2100 cm⁻¹ to highlight the present peaks. This fact might suggest a low amount of binder compared to the parent carbon, potentially signifying insufficient crush strength of the pellets that do possess some binder-derived peaks.

E. Adsorptive properties and Characteristics

The affinity of the produced pellets towards CO₂ has been evaluated on a TGA at 1 bar and 50 °C under a pure CO₂ flow of 50 mL/min. Prior to the experiments the samples have been subjected to a pure stream of N₂ at 50 mL/min at 150 °C. This was done to ensure desorption of any pre-adsorbed species from ambient air (e.g. moisture) [29].

TABLE III. EQUILIBRIUM CO₂ ADSORPTION RESULTS AT 50 °C.

Sample Name	CO ₂ Uptake, mg/g
VC powder	15.2
VCP	10.9
P-A	31.4
A-P	22.4
AC powder	33.7

As can be seen from Table III, the samples that underwent pelletization last (i.e. VCP and A-P) present a lower (by ~30%) adsorption capacity compared to their powder-from analogues. This can be associated with a lower surface area due to clogging/covering of the nanopores by the binder. On the other hand, physical activation of the carbons (both powder and pellet) facilitated a substantial increase of the CO₂ uptake. As per the influence of the production pathway on adsorptive properties, the presence of the hydroxyl groups did not necessarily assist CO₂ adsorption. Instead, the porous structure is believed to be more impactful as shown in Section C.

Additionally, all of the samples have been fitted (non-linearly) to the pseudo-first (PFO) and the pseudo-second order (PSO) kinetic models to further investigate the sorption process. This examination followed the improved methodology pathway described in [30] with the goodness of fit being evaluated *via* the regression coefficient (R²) and the normalized root mean square error (NRMSE). Interestingly, all of the samples were more accurately described by the latter model. This is to be expected for the activated carbons due to an increased presence of active adsorption sites [29]. For the VCP, on the other hand, the worse fit of the PFO model suggests adsorption not to be diffusion controlled in this case [31]. This phenomenon may stem from the very large macropores produced during pelletization (as visible in Figure 2) which could assist diffusion into the porous framework of the adsorbent.

The results of the PSO fitting are presented in Table IV.

TABLE IV. PSO MODEL KINETICS OF CO₂ ADSORPTION AT 50 °C.

Sample Name	k ₂	R ²	NRMSE
VCP	0.01054	0.9711	0.003338
P-A	0.08456	0.9495	0.003443
A-P	0.02136	0.9885	0.001635

The acquired data suggests key differences between the materials. Regardless of the production pathway, the activated samples presented improved adsorption kinetics over the VCP sample. Within that, however, the rate constant (k₂) of P-A is quadruple that of A-P. As such, the former sample is (in theory) expected to demonstrate a “steeper” breakthrough curve under dynamic adsorption conditions in a packed column. This phenomenon would maximize the use of adsorbent bed, hence, addressing a further industrial challenge of increasing the operation efficiency of the material.

F. Mechanical Properties and Crush Strength

In order to be deployed at scale, nanoporous sorbents ought to have acceptable mechanical properties. As such, investigation into the impact of the production pathway of the sorbent towards crush strength has been conducted with the results presented in Table V.

TABLE V. CRUSH STRENGTH RESULTS.

Sample Name	Crush Strength, N/mm
VCP	1.054
P-A	N/S
A-P	0.794

The order of the production pathway has had a significant effect on the resulting properties. Namely, P-A possessed a very low crush strength that could not be registered by the employed equipment. This phenomenon was associated with the organic nature of the binder, which decomposed upon activation of the extrudate leading to a brittle pellet that can easily be crumbled. As such, inorganic medium (e.g. bentonite) is suggested as the preferred alternative for the “*pelletize-then-activate*” pathway. Alternatively, other

modes of particle forming (e.g. high-pressure moulding) could potentially improve the mechanical properties of such nanoporous carbonaceous adsorbents. On the other hand, the pellets that have not undergone activation (only drying), i.e. VCP and A-P, have presented crush strengths that are comparable to other extruded carbonaceous adsorbents in the literature [32] as well as to the minimum requirement for extruded catalyst from alumina [33]. Also, as suggested previously, the virgin pellets possess a higher resistance to crushing than the A-P samples. Nevertheless, in order to find wide application in industry, the crush strength should be improved, namely to be able to withstand at least 4 N/mm [34] (yet preferably over $\sim 8 - 10$ N/mm [33], [35], [36]). Further research might evaluate the efficacy of industrial-grade extruders to attain these requirements.

IV. CONCLUSION

A comparative analysis of production pathways (i.e. the order of the pelletization and activation processes) of nanoporous sorbents has been performed. The results suggest high temperature activation to significantly improve the adsorptive characteristics, yet decrease the mechanical stability of the sorbent pellets. The greater CO₂ uptake alongside the preferable kinetics (as well as the significant advantages in terms of surface area and pore volume) of the P-A sample are associated with lesser pore blockage from the organic binder. This phenomenon, in turn, significantly reduces the crush strength of the material. As such, in order to overcome this operational challenge further research into alternative pellet/particle forming techniques as well as into alternative binders is encouraged.

The A-P samples also present improved sorption characteristics versus the VCP, i.e. doubling of both the equilibrium adsorption capacity as well as the kinetic parameters, whilst maintaining similar mechanical properties. However, further studies should be conducted in order to achieve the targets for industrial usage.

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