

Development of Nanoporosity on a Biomass Combustion Ash-derived Carbon for CO₂ Adsorption

Mikhail Gorbounov¹, Ben Petrovic¹, Serap Özmen², Peter Clough², Dilyara Bekmuratova¹ and Salman Masoudi Soltani¹

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

²Energy and Power Theme, School of Water, Energy and Environment, Cranfield University, Cranfield, MK43 0AL, United Kingdom

Abstract — Carbonaceous adsorbents are one of the most widely-used materials used for the removal of chemical species in gaseous and aqueous media. However, the route from precursor to activated carbon is riddled with myriad techniques and steps, that entail additional costs. Such expenses could be minimized *via* waste valorization e.g. biomass combustion bottom ash which has been used in this work. In order to develop surface nanoporosity, the waste-derived carbon was thermally treated, increasing the CO₂ adsorption capacity by nearly twofold and thus, producing a cost-effective sorbent for post-combustion CO₂ capture. The effectiveness of such “unconventional” activation route has been verified using Scanning Electron Microscopy, Fourier-Transform Infrared Spectroscopy as well as Proximate Analysis and the CO₂ adsorption data obtained *via* Thermogravimetric Analysis (TGA). The proposed material and method could serve as a viable alternative to the current methods for decarbonization of the UK power sector through *in-situ* waste valorization.

I. INTRODUCTION

Activated carbons (ACs) have been widely employed as sorbents for various applications, both in aqueous and gaseous media for centuries. It is believed that the ancient Sumerians and Egyptians have utilized primitive carbonaceous sorbents as early as 3750 B.C. during bronze production [1] and later on in 1500 B.C. as a medicament [2] to treat food poisoning (i.e. adsorption of various toxins) as well as adsorption of odorous vapors [3]. Nowadays, however, novel nanomaterials have a much wider range of applications and much more robust production methods, especially when considering upcycling waste to AC. Normally carbonaceous materials are converted into adsorbents *via* a two-step process. Firstly, the raw precursor is carbonized by various thermal treatment techniques leading to formation of a carbonaceous framework as opposed to a fibrous one. Then, the produced carbon is further processed (i.e. activation) to develop porosity, hence, an increased surface area. This is classically done *via* physical or chemical treatment. The former is usually carried out with steam, air or carbon dioxide, whereas, chemical activation requires addition of activating agents (H₃PO₄, H₂SO₄, ZnCl₂, K₂CO₃, KOH and myriad others). These agents etch through

the surface of the carbon, thereby creating surface heterogeneity and, potentially, surface functionalities [4]. However, such treatments increase the capital and operational expenditures (CAPEX and OPEX), hence the high cost of the adsorbent; especially when considering chemical activation, since it requires not only procurement of chemical substances but also additional washing steps to “normalize” the pH of the produced sorbent. Avoiding such expenses could lead to a more viable as well as environmentally friendly process, as the secondary pollution from the activating agents would be prevented. Lastly, equipment corrosion from steam, acids and bases used for the activation is also a cause for concern that could be mitigated if increasing the adsorption capacity of the sorbent *via* alternative routes. These monetary benefits are of utter importance when considering commercialization of novel separation processes, such as post-combustion carbon capture with solid adsorbents.

In our previous work [5], we have derived carbon from biomass combustion bottom ash (avoiding the first carbonization step normally described in waste to AC process literature). In this work, we have built upon our previously-produced sorbent, increasing its porosity, though, not by traditional activation. Herein, we have endeavored to add porosity to the bottom ash-derived carbon, as well as alleviate the carbon of the tars and other volatile organic matter present on the surface of the material. This was achieved *via* thermal treatment in an inert environment (N₂), as opposed to costly and/or eco-unfriendly classical chemical activation techniques.

II. MATERIALS AND METHODOLOGY

A. Carbonaceous Precursor Production Method

Industrial-grade biomass combustion bottom ash (BA) was used as the raw material for extraction of virgin carbon (coded name BA-63-P) following the method described in our previous work [5].

B. Nanoporosity Development

To increase the surface heterogeneity, BA-63-P (0.2 – 0.4 g) was placed in a ceramic boat. The vessel was then transferred into a tubular furnace (Carbolite Gero TF1 12), with an Inconel tube insulated with appropriate ceramic plugs for a more even temperature profile. The sample was then thermally treated under 300 ml/min of N₂ for the entire duration of the experiment. The furnace was programmed to reach the target temperature of 700 °C (with a ramping rate of 15 °C/min), at which the BA-63-P was held for 70 minutes. Afterwards, the sample was left in the furnace under the same continuous flow of nitrogen to cool down to ambient temperature. The described furnace set-up is pictured in Figure 1.



Figure 1. Tubular Furnace used for BA-63-P Activation.

The properties of AC-BA-63-P were studied *via* Fourier-Transform Infrared Spectroscopy (Perkin Elmer Spectrum One), Energy Dispersive X-ray Spectroscopy coupled with Scanning Electron Microscopy (JOEL IT200) as well as TGA (Mettler Toledo TGA 2) and Proximate Analysis. Finally, TGA was also used to compare the produced nanoporous carbon to a commercial AC (Sigma Aldrich, CAS 7440-44-0).

III. RESULTS AND DISCUSSIONS

A. Fourier-Transform Infrared Spectroscopy (FTIR)

The infrared spectrum was acquired following the attenuated total reflection method with the measurement starting at 550 cm⁻¹ and ending at 4000 cm⁻¹ with a resolution of 4 cm⁻¹. Figure 2 depicts the acquired FTIR spectrum of the sample.

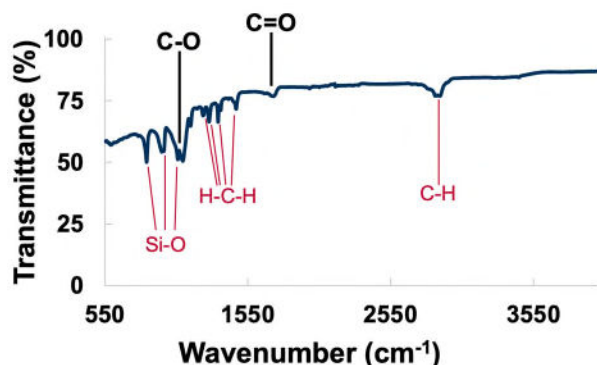


Figure 2. AC-BA-63-P Infrared Spectrum.

Numerous peaks were identified on the AC-BA-63-P. The cluster of peaks on the left side of Figure 2 were assigned to various modes of vibration of the Si-O bond present in the differently configured aluminosilicate ash impurities [6]–[8]. However, the bands at 1094 and 1147 cm⁻¹ can be alternatively assigned to the stretching vibrations of the C-O bond found, for instance, in graphene oxides [9], [10]. The wavenumber of 1467 cm⁻¹ is the characteristic of scissoring vibrations for the CH₂ group [6]. The bands below (1200 – 1360 cm⁻¹) can also be associated with the methylene group or (though not as straightforwardly as the in-plane bending described previously). Their splitting might be caused by the presence of semi-crystalline strictures within the sample [6]. Another characteristic aliphatic substituted hydrocarbon peak is visible at the wavenumber of 2862 cm⁻¹ [9], [10] and the band at 1731 cm⁻¹ was ascribed to the C=O bond [6], [8].

B. Energy Dispersive X-ray Spectroscopy (EDS)

The EDS results are presented in Table I.

TABLE I. ELEMENTAL COMPOSITION OF AC-BA-63-P AND THE PARENT BA-63-P.

AC-BA-63-P		Virgin BA-63-P	
Element	Weight %	Element	Weight %
C	27	C	75.8
O	72.3	O	21.4
Al	< 0.1	Al	0.7
Si	0.2	Si	0.6
K	< 0.1	K	0.5
Ca	0.4	Ca	1
This work		[5]	

As seen here, a significant amount of elemental carbon has been lost during the thermal treatment when compared to the parent BA-63-P data [5]. This is to be expected since at elevated temperatures, decomposition of less stable surface functionalities occurs as well as general thermal degradation of the carbonaceous sorbent. The differences in the mineral matter quantities in Table I could be associated with material variation as discussed in *Section III. D*.

C. Scanning Electron Microscopy (SEM)

The impact of thermal treatment on the morphology of the sample was studied using SEM. The development of heterogeneity upon activation is clearly visible in Figure 3 and Figure 4.

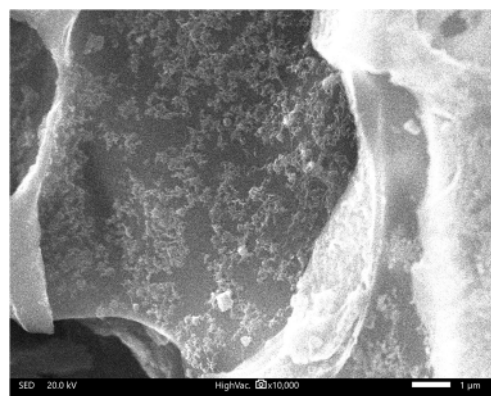


Figure 3. AC-BA-63-P under magnification of 10,000x.

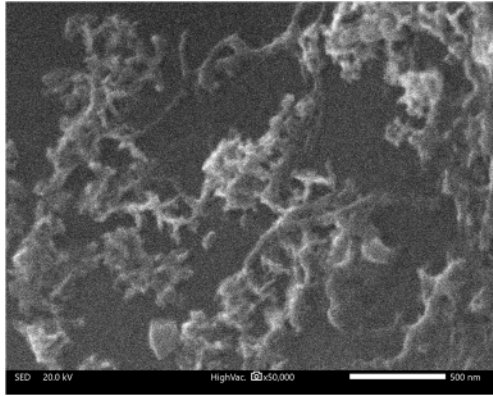


Figure 4. AC-BA-63-P under magnification of 50,000x.

The pristine BA-carbon did not possess a developed nanoporous structure, hence, the lower surface area and CO₂ uptake. Additionally, the aluminosilicate impurities present in the sample (as suggested by analysis techniques from *Section III. A* and *III. B* as well as the data on the parent-material) have not been impacted in any meaningful way by the thermal treatment. Their amorphous structure and spherical shape are typical for ashes. These particulates are scattered within the bulk of AC-BA-63-P and are not shown in Figure 3 and Figure 4 due to the SEM analysis being focused on porosity development on the virgin carbon (they are, however, clearly visible in our previous work [5]).

D. Proximate Analysis

As evident from the proximate analysis results (Table II), the amount of volatile organic compounds (VOCs) in the improved sorbent has significantly decreased, when comparing to the original virgin BA-derived carbon. This phenomenon can be readily explained by the thermal treatment conducted on the carbon, during which the VOCs have escaped from the surface of the adsorbent (a noted previously in *Section III. B*), hence, increasing its porosity.

Additionally, the produced nanoporous material had a lower fixed carbon content than a commercial activated carbon (Comm-AC), that was used as a benchmark for this study, but a less moisture uptake, suggesting higher hydrophobicity of AC-BA-63-P. The latter quality is of utter importance when considering industrial implementation of post-combustion carbon capture from biomass combustion flue gas. Moisture may competitively adsorb on the surface on the carbon, thereby decreasing the CO₂ uptake. The decreased values, alternatively, could be explained by a higher ash content of AC-BA-63-P, leading to a “skew” towards lower numbers for these dependent variables of the proximate analysis.

TABLE II. PROXIMATE ANALYSIS RESULTS

Sample name	Moisture, wt%	VOC, wt%	Fixed C, wt%	Ash, wt%	Reference
BA-63-P	6	35	52	7	[5]
BA-63-P	5	30	50	15	This work
AC-BA-63-P	1.5	6	72.5	20	This work
Comm-AC	5	4	85	6	This work

On a separate note, when comparing to the virgin material to the sample evaluated in our previous work, the ash content is substantially higher (hence, the lower proportion of the Fixed C, VOCs and H₂O). It has been learned that the observed variation in ash content is associated with a different boiler and/or combustion conditions at the power plant, where the raw precursor was collected. As such, the BA-63-P described in [5] has a lower ash content, whereas, the carbon content is less, in turn, a higher CO₂ uptake at 25 °C and ambient pressure under a stream of pure CO₂ (discussed in *Section III. E*). However, the variation in adsorption capacity (at the described above conditions) is rather minute: going from 0.73 mmol/g (32.2 mg/g) to 0.67 mmol/g (29.5 mg/g), whereas, the impact of the “unconventional” activation was much more pronounced.

E. Adsorptive Properties and Characteristics

The CO₂ adsorption capacity has been evaluated *via* TGA and is discussed below. AC-BA-63-P has shown significant potential for carbon dioxide adsorption at not only ambient conditions but also at temperatures closer to the post-combustion setting. The activation process allowed the uptake to double at 75 °C and to nearly double at both 25 and 50 °C under atmospheric pressure and pure CO₂. This phenomenon can be attributed to pore de-clogging of the sorbent (as opposed to conventional pore etching and/or widening) during the thermal treatment under N₂.

Furthermore, when comparing the investigated material to Comm-AC, similar adsorption capacities can be observed. It is noteworthy that inlet temperatures of post-combustion capture units for power-plant flue gases are approximately 50 °C, hence, the CO₂ uptake at this temperature is, perhaps, a more valuable metric than the often-quoted adsorption capacities at 25 °C. As can be inferred from Table III, the produced AC-BA-63-P is a competitive alternative to its commercial analogues with better performance at elevated temperatures. Additionally, the adsorption capacity of the produced nanoporous carbon is comparable to other biomass combustion ash-derived sorbents [11].

TABLE III. ADSORPTION CAPACITY OF THE EVALUATED MATERIALS

Sample	Uptake at 25 °C, mmol/g	Uptake at 50 °C, mmol/g	Uptake at 75 °C, mmol/g
BA-63-P	0.67	0.38	0.19
AC-BA-63-P	1.11	0.70	0.43
Comm-AC	1.23	0.68	0.40

F. Yield of Final Product

Thermal treatment under nitrogen resulted in a decrease in the mass of final product (as per the phenomena described in *Sections III. B* and *III. D*). However, when compared to other carbonaceous nanoporous sorbents (regardless of the precursor or activation method) available in the literature [12], AC-BA-63-P is on the higher end (and exceeding most) of the reported values with the yield of 64.26%. Such results even surpass the yields of some commercial-grade ACs [13].

IV. CONCLUSION

Biomass Combustion Bottom Ash-derived carbon has been thermally treated in an inert atmosphere to increase its surface heterogeneity. As a result, the carbon has lost most of its volatile organic compounds. Nevertheless, the development of nanopores has been clearly evidenced *via* SEM imaging and, most importantly, the CO₂ adsorption capacity. The uptake of carbon dioxide by the nanoporous sorbent has nearly doubled across the evaluated temperature range. Additionally, the low cost of precursor and the activation method, as well as lack of secondary pollution from chemical activating agents or from landfilling of the bottom ash make such approach even more attractive for the decarbonization of the UK biomass combustion sector. Finally, the yield of the AC product has been shown to be remarkably high, thus, constituting another benefit of such procedure.

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