Adsorption of hydrogen sulphide on activated carbon materials derived from the solid fibrous digestate

E. Choleva [1,2], A. Mitsopoulos [1], G. Dimitropoulou [1], S. Patsatzis [4], G. Romanos [2], E. Kouvelos [2], G. Pilatos [2], S. Stefanidis [3], A. Lappas [3], T. Sfetsas [1]

[1] QLAB Private Company, Research & Development, Quality Control and Testing Services, Thessaloniki, 57008 Greece; t.sfetsas@q-lab.gr
[2] Institute of Nanoscience and Nanotechnology, National Center of Scientific Research "Demokritos", Agia Paraskevi, Athens, 15310, Greece; g.romanos@inn.demokritos.gr
[3] Laboratory of Environmental Fuels/Biofuels and Hydrocarbons, Chemical Process and Energy Resources Institute, CERTH, Thessaloniki, 57001, Greece; angel@cperi.certh.gr
[4] Biogas Lagada SA, 677 Parcel, Kolchiko, Lagadas, 57200, Greece; s.patsatzis@biogaslagada.gr
Keywords: activated carbon; hydrogen sulphide removal, biogas, carbonization, solid fibrous digestate.
* Presenting author email: choleva.evangelia@gmail.com

The main goal of this work is to develop a sustainable value chain of carbonaceous adsorbents that can be produced from the solid fibrous digestate (SFD) of biogas plants and further applied in integrated desulphurisation-upgrading (CO_2/CH_4 separation) processes of biogas to yield high purity biomethane. On this purpose, physical and chemical activation of the SFD derived biochar was optimised to afford micro-mesoporous activated carbons (ACs) of high BET surface area (590-2300 m^2g^{-1}) and enhanced pore volume (0.57-1.0 cm^3g^{-1}). Gas breakthrough experiments from fixed bed columns of the obtained ACs, using real biogas mixture as feedstock, unveiled that the physical and chemical activation conclude to different types of ACs which are sufficient for biogas upgrade and biogas desulphurisation respectively. Performance assets of the samples such as the CO_2 and H_2S adsorption capacity and the H_2S/CO_2 selectivity were elaborated in relation to the pore structural (pore size, narrow or wide pore size distribution, existence of mesopores) and surface (specific surface, surface chemistry) characteristics of the samples to unveil the crucial properties that determine the selectivity for CO_2 or H_2S. Moreover, performing breakthrough experiments at three temperatures close to ambient it was possible to calculate the steric heat of sorption and define the optimum conditions for enhanced H_2S/CO_2 separation. It was also concluded that the H_2S adsorption capacity is significantly affected by restriction to gas diffusion. Hence, the best performance was obtained at 50°C and the maximum observed in the H_2S adsorption capacity vs the temperature is attributed to the counterbalance between adsorption and diffusion into micropores.

As a general outcome of this work, it is concluded that when the target is to upgrade biogas, both type of materials, (physically and chemically activated carbons from SFD biochar), can be used since both have the capacity to adsorb significant amounts of CO_2 and H_2S that reach values above 2 mmol/g at ambient temperature and biogas pressure of 1 bar. Due to the minor effect of physical activation on the integrity and population of the AC's surface functional groups, the physically activated samples exhibit very high H_2S adsorption selectivity over CO_2 and can be involved in a pre-treatment desulphurisation process upstream the main biogas upgrade process (CO_2/CH_4 separation).

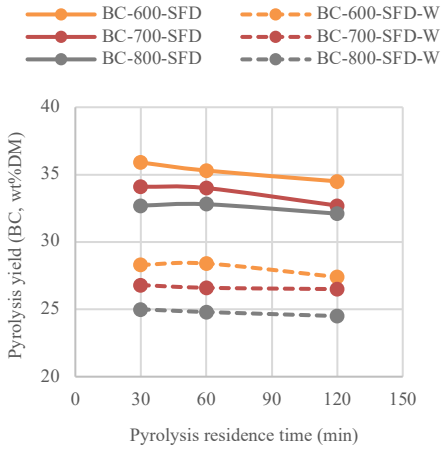

Figure 1. Biochar yields

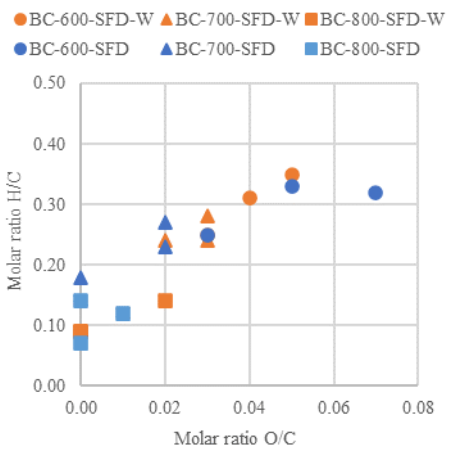

Figure 2. Van Krevelen diagram

The experimental procedure involved filtration (in a filter press) of the whole digestate from the anaerobic digester of a biogas plant (Biogas Lagadas), followed by a drying stage to obtain the SFD (solid fraction of digestate) at a yield of about *25%wt.* Next, the removal of the inorganic content was achieved via washing of the SFD precursor with HNO_3 solution (1% v/v). The washed precursors are following abbreviated as SFD-W. The

carbonization was carried out in a bench scale fixed bed reactor investigating the effect of the maximum carbonisation temperature (600-800ºC) along with the duration of the isothermal stage (30-120mins). Taking into account the biochar yield % wt. DM, pyrolysis temperature of 600ºC has the highest yield compared to higher ones while residence pyrolysis time seems to not affect the biochar yield, noticing that shorter duration of pyrolysis (30mins) has given the optimal yield for the biochar sample, [Figure 1]. Van Krevelen diagram, [Figure 2], shows increasing the pyrolysis temperature, decreases the H/C ratio, which indicates the increased aromatization and decarbonization of the biochar. Furthermore, decreased ratio H/C and O/C when increasing the pyrolysis temperature indicates the reduced hydrophilicity of the biochar's surface, (Stefaniuk and Oleszczuk, 2015).

Biochar materials derived from the carbonization of SFD (BC-SFD) had very low BET specific surface area (<50 m^2g^{-1}) compared to biochar samples obtained from SFD-W (BC-SFD-W) (up to 363 m^2g^{-1}); the ash content of the BC-SFD samples was higher (more than 33.60%) and rather lower for the BC-SFD-W materials (up to 18.10%). This indicates the removal of part of the inorganic compounds (~72%) on the surface of the precursor material with the HNO_3 pre-treatment. The biochar BC-SFD-W yields 24.5-28.4%wt. DM. Biochar obtained by SFD-W produced activated carbon Activated carbons were obtained by biochar materials derived from SFD-W precursor investigating types of activation; physical and chemical. Biochar was physically activated with H_2O investigating the activation parameters of temperature (700-900ºC), flow rate of the carrier gas (0,5-1,5 mL/min) and residence time (15-90mins) and chemically with KOH testing the temperature (600-800ºC), KOH/biochar ratios (1:1-4:1) and residence time (30-120mins). Micro-mesoporous carbonaceous materials were obtained, with BET surface areas between 585 and 2299 m^2g^{-1} and pore volumes between 0.569 and 1.010 cm^3g^{-1}, [Table 1].

Table 1. Surface and pore characteristics of the biochar and activated carbon materials.

Sample	BET (m^2/g)	Pore size (m^2/g)	Specific Surface area (m^2/g)	Micropore Volume (cm^3/g)	Total pore Volume (cm^3/g)
BC-600-30mins-SFD	18	10	8	0.004	0.021
BC-600-30mins-BC-SFD-W	279	263	16	0.103	0.125
AC-H_2O800-BC600-30mins-SFD-W	585	220	366	0.095	0.569
AC-KOH800-BC600-30mins-SFD-W	2299	2174	125	0.887	1.010

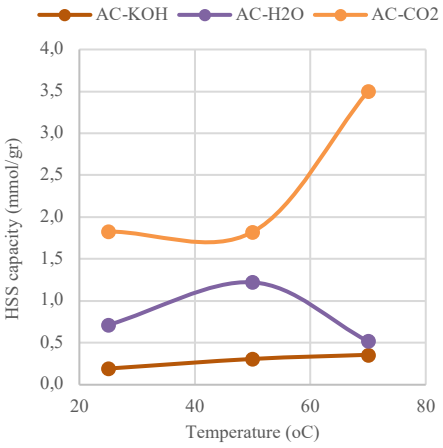

Figure 3. H_2S capacity of the activated carbons

The inlet concentration of H_2S was 500 ppm and the inlet flow of the synthetic biogas was 50mL/min. Biogas synthesis was 57% CH_4, 42% CO_2, 0.5% O2 and 500ppm H_2S. The outlet H_2S and CO_2 concentrations in the synthetic biogas stream were continually measured by detectors. When the concentration of H_2S in the effluent gas reached about 50% of its inlet value (C/C_0=0.5), the adsorption reaction was considered completed. The adsorption of the CO_2 is concluded in less than 500seconds due to its high concentration (~$4 \cdot 10^5$ppm). The reactor is fully loaded per volume (AC samples weighted from 0.15 up to 0.30g) with the activated carbon sample to be evaluated and prior to all the tests carried the samples were degassed at 250ºC for 12h. The adsorption capacity was calculated by integrating the area above the breakthrough curve for the given inlet H_2S concentration of 500ppm, the mass of the adsorbents-AC and the inlet flow settled at 50mL/min. The higher the specific surface area the more H_2S is adsorbed from the activated carbon while the higher the BET specific surface area the more CO_2 is adsorbed. This indicates that the anchoring of the H_2S molecules happens on the outer surface of the carbon and the CO_2 molecules anchor iside the pores of the carbon. Activated carbon AC-H_2O has lower BET surface area than AC-CO_2 and adsorbs more H_2S at 50ºC and less at 70ºC while activated carbon AC-CO_2 adsorbs the most H_2S at 70ºC, [Figure 3]. The highest selectivity of hydrogen sulfide adsorption over CO_2 is achieved for 70ºC, followed by 50ºC adsorption temperature on the activated carbon physically functionalized with CO2; $2.3 \cdot 10^4$ and $1.5 \cdot 10^4$ respectively.

References

Stefaniuk M, Oleszczuk P., (2015). Characterization of biochars produced from residues from biogas production, *J Anal Appl Pyrol. 115 (2015) 157–165*. https://doi.org/10.1016/j.jaap.2015.07.011

Acknowledgements

This research was co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code: T2EDK-00455 PYRO-D).