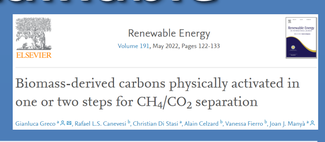
Improving biogas quality by CH_4/CO_2 separation: the pivotal role of sustainable biomass-derived activated carbons.



Gianluca Greco[a], Rafael L. S. Canevesi[b], Christian Di Stasi[a], Alain Celzard[b], Vanessa Fierro[b], Joan J. Manyà[a]

[a] *Aragón Institute of Engineering Research (I3A), Thermochemical Processes Group, University of Zaragoza, Escuela Politécnica Superior, crta. Cuarte s/n, Huesca E-22071, Spain.*

[b] *Université de Lorraine, CNRS, IJL, Épinal F-88000, France*

greco@unizar.es

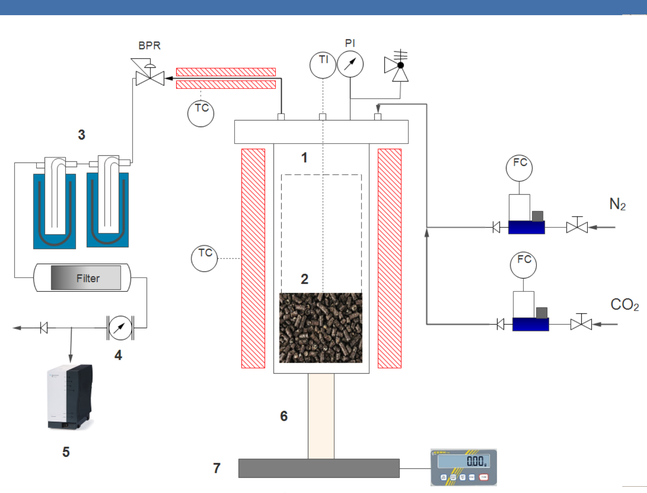
Introduction

Among all the available technologies for biogas upgrading, one of the most promising due to its relatively low cost and high energy efficiency is CO_2 separation by adsorption. For this purpose, biomass-derived activated carbons (ACs) are considered interesting candidates, presenting many advantages such as high CO_2 adsorption capacity or low costs related to their production and regeneration. When used in biogas upgrading applications, ideal ACs should exhibit high selectivity towards CO_2, guaranteed by appropriate pore size distribution and surface chemistry. As an alternative to conventional two-step production process mentioned above, biomass-derived ACs can also be synthesized by a one-step thermochemical process, considered to be a very interesting solution in terms of energy recovery, especially for large-scale production systems.

Objective

The aim of the present study is to contribute to fill the gaps that still exist in establishing the most suitable route for the conversion of biomass feedstock into ACs with tuned porosity. To this end, several wheat straw-derived ACs were prepared by two-step and one-step activation processes under different operating conditions (maximum temperature, absolute pressure and CO_2 content in the carrier gas). The most promising ACs (i.e., those with the best textural properties for CO_2 adsorption from both one-step and two-step conversion processes) were then tested as selective adsorbents for CO_2/CH_4 separation.

Experimental



Pyrolysis set up.

Activation set up.

Biomass feedstock

Wheat straw (WS) pellets were used as raw feedstock. The as-received biomass was directly pyrolyzed without any preliminary milling step in order to maximize the final carbonization efficiency.

One-step activation

The one-step activation process was performed using the same bench-scale fixed-bed reactor described in a previous work [1].

Two-step activation

The pyrolysis step was performed using the same bench-scale fixed-bed reactor as for the one-step activation. All biochars obtained after pyrolysis were then physically activated at 800 °C and atmospheric pressure under a pure CO_2 atmosphere in a lab-scale activation plant [2].

Adsorption isotherms

CO_2 and CH_4 adsorption isotherms were measured up to 3.5 MPa, at 25 and 50 °C. The experimental data obtained from the isotherms were described using the Sips model. The ideal adsorbed solution theory (IAST) was adopted to predict the adsorption behavior of CO_2/CH_4 binary mixtures at different volume concentrations.

$$Selectivity\ (S) = (x_{CO_2}\, y_{CH_4}) / (x_{CH_4}\, y_{CO_2})$$

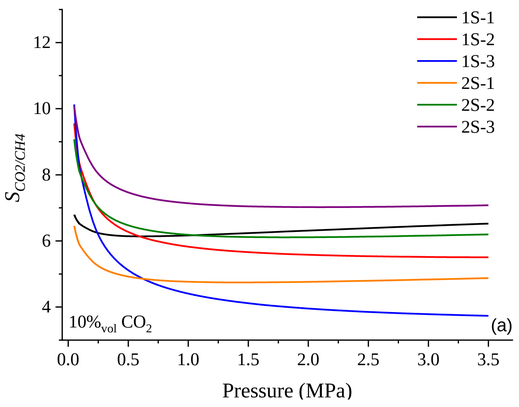
Type of activation	AC	Slow Pyrolysis T (°C)	P (MPa)	τ (s)	CO_2 (vol. %)	CO_2 activation T (°C)	P (MPa)	τ (s)	CO_2 (vol. %)
One-Step	*1S-1*	-	-	-	-	700	0.55	100	37.5
	1S-2	-	-	-	-	750	0.2	100	75
	1S-3	-	-	-	-	750	0.9	100	75
Two-Step	*2S-1*	400	0.2	100	60	800	0.1	-	100
	2S-2	400	0.2	200	0	800	0.1	-	100
	2S-3	400	0.2	200	60	800	0.1	-	100

Results

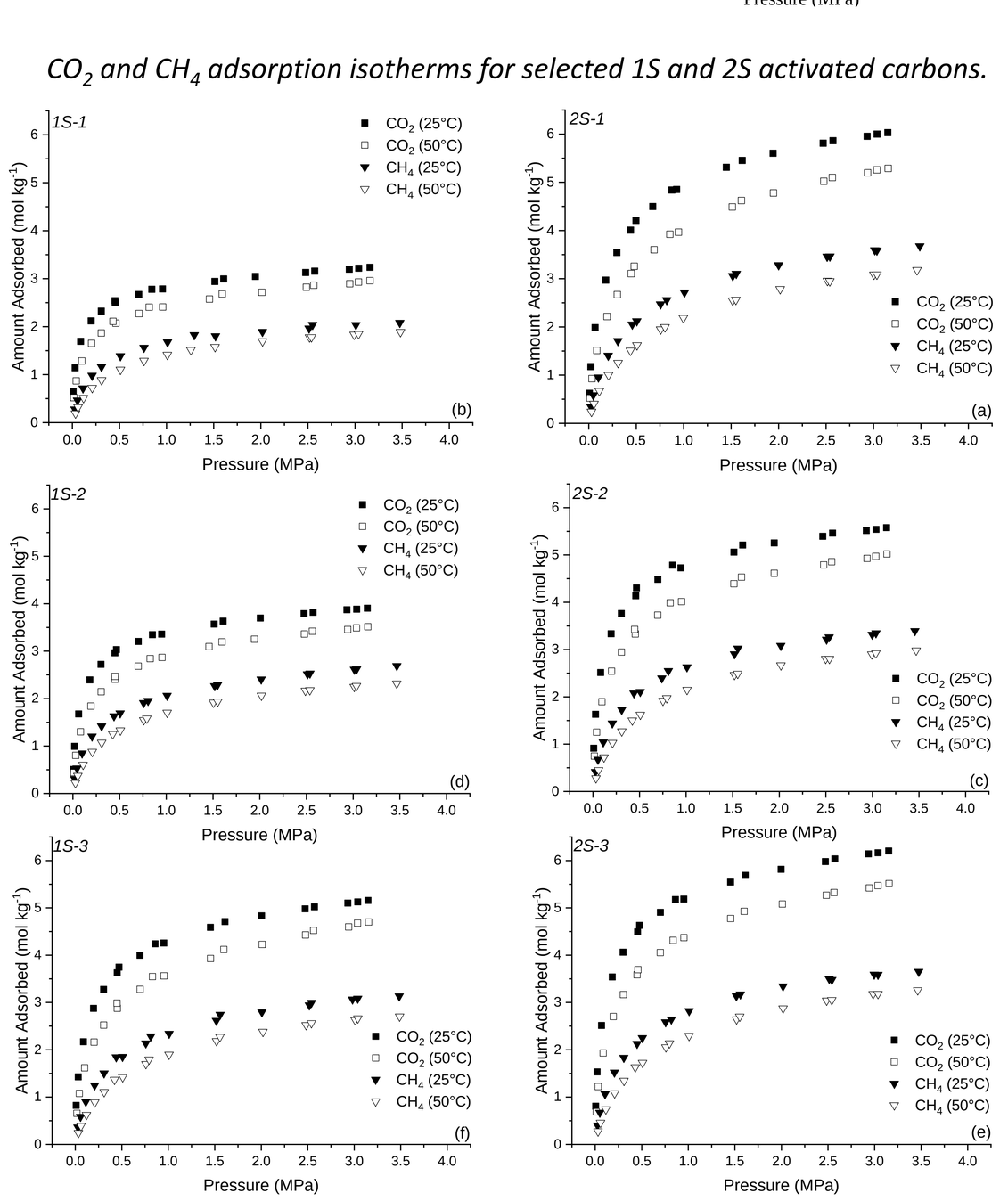
Textural characterization of the produced activated carbons.

#	$S_{2D\text{-}NLDFT}$ ($m^2\,g^{-1}$)	V_{micro} ($cm^3\,g^{-1}$)	V_{meso} ($cm^3\,g^{-1}$)	V_{ultra} ($cm^3\,g^{-1}$)
1S-1	700	0.15	0.02	0.14
1S-2	760	0.19	0.01	0.14
1S-3	882	0.26	0.02	0.14
2S-1	986	0.30	0.05	0.11
2S-2	957	0.26	0.02	0.18
2S-3	998	0.28	0.02	0.17

IAST-based selectivity values for ACs tested under 10 vol. % CO_2.



CO_2 and CH_4 adsorption isotherms for selected 1S and 2S activated carbons.



References

1. G. Greco, C. Di Stasi, F. Rego, B. González, J.J. Manyà, Effects of slow-pyrolysis conditions on the products yields and properties and on exergy efficiency: A comprehensive assessment for wheat straw, Appl. Energy. 279 (2020). https://doi.org/10.1016/j.apenergy.2020.115842.
2. C. Di Stasi, G. Greco, R.L.S. Canevesi, M.T. Izquierdo, V. Fierro, A. Celzard, B. González, J.J. Manyà, Influence of activation conditions on textural properties and performance of activated biochars for pyrolysis vapors upgrading, Fuel. 289 (2021) 119759. https://doi.org/10.1016/j.fuel.2020.119759.

Conclusions

- Both *1S* and *2S* ACs exhibited even higher CO_2 uptakes and CO_2/CH_4 selectivity values than several adsorbents reported in the literature.
- One-step physical activation at moderate pressure resulted to be a promising route to produce carbon-based adsorbents, which may replace the conventional two-step physical activation process and lead to remarkable improvements, especially on an industrial scale.
- One-step physical activation would allow a significant reduction in operating and installation costs as well as an improvement in productivity.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 721991
http://greencarbon-etn.eu/