

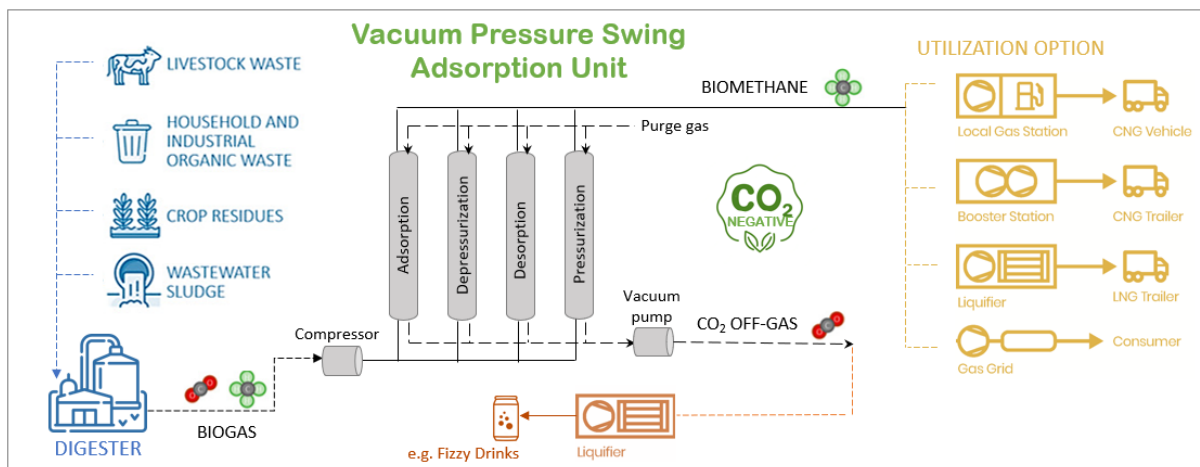
Optimizing Vacuum Pressure Swing Adsorption for High-Efficiency Biomethane Production



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Graphical Abstract



The current global energy and climate crisis has significantly pushed research and technological development toward energy production from renewable and sustainable sources. Biofuels offer a viable alternative to address the growing scarcity of fossil fuels, pressing energy demand, and climate change risks (Wang et al., 2021). Thanks to such drivers, biofuel production is experiencing a moment of remarkable research, innovation, and development, and it is expected that by 2050 they could supply about a quarter of the world's energy needs (Ahmed et al., 2021).

Biogas from anaerobic digestion of organic matter (a mixture of 50-80% CH₄, 20-50% CO₂, and other trace components) is a valuable energy carrier, a renewable and sustainable fuel, potentially obtainable from agricultural biomass (dedicated crops, agricultural waste, and animal manure), agro-industrial waste (food processing chain waste), and the organic fraction of municipal solid waste (FORSU). Biogas can be used as a fuel as is (to produce electricity and thermal energy), downstream of purification operations, or be subjected to a further upgrading process, i.e., separation of carbon dioxide, resulting in an increase in calorific value and the obtaining of biomethane capable of entirely replacing natural gas derived from fossil fuels. The energy carrier biomethane has the lowest C/H ratio of any transition fuel. It is fully compatible with existing natural gas transportation and storage infrastructure and equipment, making it suitable for all domestic, industrial, and transportation energy needs. Biomethane plays a crucial role in addressing the global energy and climate crisis, exemplifying the circular economy by completely recovering organic waste as an energy source (D'Adamo et al., 2021; Kapoor et al., 2020). Its development positively impacts the agribusiness sector, promoting an economic model based on sustainability and circularity in the use of resources (food & fuel farm model) that reduces agricultural emissions (up to 14%) and returns organic matter to the soil (via digestate). Additionally, biomethane production from FORSU contributes to closing the waste cycle, offering benefits in terms of renewable energy production, decarbonization, and air pollution control. Currently, biomethane production in Italy stands at approx. 280 Mcm (GSE), with production potential to 2030, could reach 8 to 10 Bcm (CIB).

Among the technologies available for upgrading biogas to biomethane, Pressure Swing Adsorption (PSA) holds great potential for its effectiveness and low capital cost, providing safety, robustness (especially in impurities), and ease of operation (Adnan et al., 2019; Khan et al., 2021; Aghel et al., 2022). Pressure Swing Adsorption (PSA) technology is a gas separation method based on adsorption operation. It takes advantage of the interactions between gas molecules and the adsorbent, which selectively retains specific molecules under different pressure and temperature conditions. The selectivity of separation depends on the type of adsorbent material used and the adsorption conditions. In upgrading to biomethane (CO₂ removal) from a biogas stream, the plant configuration involves passing the biogas stream to purify

through a column containing a fixed bed of porous material. The CO₂ molecules, which are present in the raw biogas stream, are retained by the adsorbent material, allowing their separation, and thus enriching the methane content of the gaseous stream. When the adsorbent material becomes saturated, the desired purity specifications of the produced biomethane stream can no longer be guaranteed. Therefore, CO₂ molecules are desorbed from the column through bed regeneration. The adsorption phase takes place at a pressure of 4-10 bar, while desorption is carried out by decreasing the pressure to the atmospheric pressure value or using vacuum pumps, reaching a minimum pressure of 0.1-0.2 bar (Abd et al., 2021); Vacuum Pressure Swing Adsorption is the term used in this operation.

Because of the cyclic nature of the separation process (adsorption-desorption), PSA units have multiple packed columns operating in parallel and out of phase with each other to operate continuously and increase plant productivity by alternating the adsorption and regeneration phases in the various beds. In this way, when the adsorbent material in the column becomes saturated, the raw biogas flow is interrupted from the first column and directed to a second column where the adsorbent material has been regenerated. Typically, three, four, or six columns are installed working in parallel, each operating at a different cycle stage. The basic configuration of the PSA process is represented by the "Skarstrom cycle" which involves alternating four phases in each column, along with the adsorption/desorption phases, the intermediate phases of pressurization (pre-adsorption) and purging (post-desorption) are also included. The selection of an appropriate adsorbent in PSA design is critical due to its impact on process efficiency (Ruthven 1984). The most promising classes of adsorbents for upgrading biogas to biomethane are carbon molecular sieves (CMSs), zeolites, and metal organic frameworks (MOFs), which offer good performance in terms of selectivity toward CO₂, adsorption capacity, and regenerability (Aghel et al., 2022). Selectivity and efficient CO₂ adsorption are the critical parameters for maximizing methane purity and recovery. Desorption rate is equally important, especially when feeding some of the valuable product for adsorbent bed regeneration, which strongly impacts CH₄ recovery. Most PSA process engineering is based on designing a protocol for adsorbent regeneration that can consume the smallest amount of energy (reduce energy expenditure) and do so in the fastest way possible (increase productivity) (Grande et al., 2011). The PSA process is very flexible in design (Shah et al., 2021). It can be further modified with additional steps (e.g., pressure equalization between the column that depressurizes and the one that pressurizes) and operated with a variable number of columns (not coincident with the number of steps they go through) to be able to optimize technical (CH₄ purity and recovery) and economic aspects. The PhD work aims to optimize the PSA cycle by identifying an efficient adsorbent material, defining the optimal process configuration, and optimizing the cycle steps and parameters to maximize CH₄ recovery and operational efficiency.

Abd, A. A., Othman, M. R., Naji, S. Z., & Hashim, A. S. Methane enrichment in biogas mixture using pressure swing adsorption: process fundamental and design parameters. *Materials Today Sustainability*, 11, 100063 (2021).

Adnan, A. I., Ong, M. Y., Nomanbhay, S., Chew, K. W., & Show, P. L. Technologies for biogas upgrading to biomethane: A review. *Bioengineering*, 6(4), 92 (2019).

Aghel, B., Behaein, S., Wongwises, S., & Shadloo, M. S. A review of recent progress in biogas upgrading: With emphasis on carbon capture. *Biomass and Bioenergy*, 160, 106422. (2022).

Aghel, B., Behaein, S., & Alobiad, F. CO₂ capture from biogas by biomass-based adsorbents: A review. *Fuel*, 328, 125276 (2022).

Ahmed, S.F., Mofijur, M., Tarannum, K. et al. Biogas upgrading, economy and utilization: a review. *Environ Chem Lett* 19, 4137–4164 (2021).

D'Adamo, I., Falcone, P. M., Huisingsh, D., & Morone, P. A circular economy model based on biomethane: What are the opportunities for the municipality of Rome and beyond?. *Renewable Energy*, 163, 1660-1672 (2021).

Grande, C. A. Biogas upgrading by pressure swing adsorption. *Biofuel's engineering process technology*, 65-84 (2011).

Kapoor, R., Ghosh, P., Kumar, M., Sengupta, S., Gupta, A., Kumar, S. S., & Pant, D. Valorization of agricultural waste for biogas based circular economy in India: A research outlook. *Bioresource Technology*, 304, 123036 (2020).

Khan, M. U., Lee, J. T. E., Bashir, M. A., Dissanayake, P. D., Ok, Y. S., Tong, Y. W., & Ahring, B. K. Current status of biogas upgrading for direct biomethane use: A review. *Renewable and Sustainable Energy Reviews*, 149, 111343 (2021).

Ruthven DM (1984) *Principles of Adsorption and Adsorption Processes*. New York: Wiley.

Shah, G., Ahmad, E., Pant, K. K., & Vijay, V. K. Comprehending the contemporary state of art in biogas enrichment and CO₂ capture technologies via swing adsorption. *International Journal of Hydrogen Energy*, 46(9), 6588-6612 (2021).

Wang, F., Harindintwali, J. D., Yuan, Z., Wang, M., Wang, F., Li, S., & Chen, J. M. Technologies and perspectives for achieving carbon neutrality. *The Innovation*, 2(4), 100180 (2021).

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