

Simulation-based design of pressure swing adsorption for methane and nitrogen separation in biogas upgrading

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Abstract

This study evaluates the performance of three adsorbents, ETS-4, MSC 3K 172, and Norit RB3, for a 68/32 %vol CH₄/N₂ separation in biogas upgrading, using a two-stage Pressure Swing Adsorption (PSA) system modeled in Aspen Adsorption. Sensitivity analysis indicated that adsorption pressure, desorption pressure and adsorption time significantly influence methane recovery and product purity. Among the materials tested, ETS-4 demonstrated the highest N₂ selectivity and most favorable breakthrough behavior, followed by MSC 3K 172 and Norit RB3. Under optimized conditions, ETS-4 achieved up to 85% CH₄ recovery at 81% purity. These results provide a robust benchmark for the development of high-efficiency PSA-based upgrading systems.

Keywords: PSA cycle optimization, Biogas upgrading, CH₄/N₂ separation, Kinetic-selective adsorbents.

1. Introduction

Climate change and resource scarcity are among today's most critical global challenges, driving the need for sustainable energy strategies [1,2]. At the international level, climate neutrality targets set by the European Climate Law and the Renewable Energy Directive promote renewable energy recovery from waste streams, including landfill gas (LFG). However, landfills remain a major source of CH₄ emissions, accounting for 3–19% of global CH₄ releases, due to long-term biogas leakage [3]. Typically, LFG contains 45–60% CH₄, 25–45% CO₂, and 2–5% N₂ [4]. Given CH₄'s high global warming potential (GWP=28) and energy content, its recovery provides both environmental and energetic advantages. Among various upgrading technologies, pressure swing adsorption (PSA) and vacuum PSA (VPSA) stand out as compact and energy-efficient solutions [5]. However, separating CH₄ from N₂, is still particularly challenging due to their similar molecular sizes (3.64 Å for N₂, 3.80 Å for CH₄), leading to limited selectivity in traditional adsorbents. While zeolites and activated carbon perform well in N₂-rich mixtures [6], CH₄-rich streams require N₂-selective adsorbents to maximize methane recovery.

Promising kinetically or size-selective adsorbents - like molecular carbon sieves (MCSs) [7] and Engelhard Titanosilicate ETS-4 [8] - have emerged. MCSs favor faster N₂ adsorption, while ETS-4 enables size-based separation, though its thermal stability is limited. Despite good N₂ selectivity, these materials often show lower equilibrium capacities than traditional adsorbents. This study evaluates three adsorbents - MSC 3K 172, ETS-4, and Norit RB3 - for separating a binary CH₄/N₂ mixture (68% CH₄, 32% N₂), in a simulated two-stage PSA process. Literature data on equilibrium, kinetics, and heat of adsorption [9] were used to identify the most effective material for maximizing CH₄ recovery under realistic operational conditions.

2. Methodology

Key physical properties of the studied adsorbent, including bulk density, particle radius, and porosities, were collected from the literature. Adsorption isotherms for CH₄ and N₂ were regressed using the Langmuir model to derive equilibrium parameters for simulation. Breakthrough behavior was analyzed using Aspen Adsorption on a 68% CH₄, 32% N₂ binary mixture. Breakthrough time, defined as the moment when N₂ at the outlet reached 5% of the inlet concentration, was used to determine optimal cycle durations.

Each material's curve provided insight into kinetic and equilibrium selectivity, with ETS-4 and MSC 3K 172 outperforming Norit RB3 in delayed breakthrough and sharper concentration fronts.

The PSA process was modeled as a two-column cycle in Aspen AdsorptionTM (Figure 1), with each bed alternating among pressurization, adsorption, depressurization, and purge.

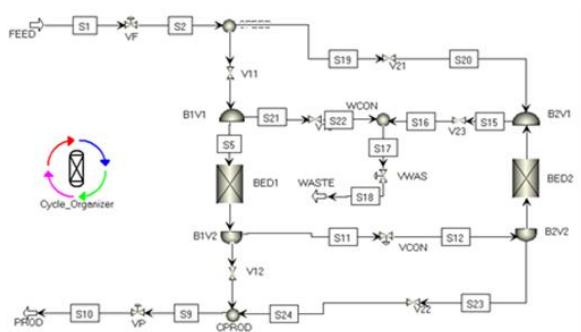


Figure 1. Process configuration modeled in Aspen Adsorption.

The system used the built-in Cycle Organizer to manage valve operation and timing. A one-dimensional plug flow model with axial dispersion was adopted, assuming isothermal conditions, ideal gas behavior, and thermal equilibrium. Intra-particle mass transfer was modeled via the Linear Driving Force (LDF) approach. Pressure drops were calculated using the Ergun equation. Multicomponent adsorption was represented using the Extended Langmuir III isotherm. Dynamic simulations were performed for each adsorbent to assess performance in terms of CH₄ recovery (R) and purity (P) reported in Eq. 1.

$$R = \frac{n_{CH_4}^{PROD}}{n_{CH_4}^{FEED}} * 100 ; P = \frac{n_{CH_4}^{prod}}{n_{tot}^{prod}} * 100 \quad \text{Eq. 1}$$

Key process parameters, such as adsorption pressure (P_{ads}), desorption pressure (P_{des}), adsorption time (t_{ads}), desorption time (t_{des}), and valve settings, were varied to optimize the cycle configuration.

3. Results and Discussion

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Breakthrough simulations for a 68/32 vol % CH₄/N₂ mixture showed that ETS-4 had the most delayed breakthrough, indicating higher N₂ adsorption capacity and slower CH₄ diffusion. MSC 3K 172 followed, with a more gradual concentration front, while Norit RB3 showed the fastest breakthrough and the steepest front, suggesting rapid saturation and limited retention. These results highlight the superior kinetic and equilibrium selectivity of ETS-4 and MSC 3K 172 toward N₂. Sensitivity analysis revealed that increasing P_{ads} improved separation by enhancing selective adsorption, while excessively low desorption pressures P_{des} did not significantly improve recovery. Adsorption time t_{ads} emerged as a critical parameter: values close to 95% of breakthrough time avoided early N₂ leakage. Too short cycles underutilized adsorbent capacity, while longer cycles reduced purity. Purge optimization via valve control improved desorption efficiency. Under optimized conditions, ETS-4 achieved up to 85% CH₄ recovery with 82% CH₄ purity, significantly outperforming both MSC 3K 172, which reached 76% recovery and 80% purity, and Norit RB3, which delivered only 74% recovery and 66% purity under optimized operating.

4. Conclusion

This study compared ETS-4, MSC 3K 172, and Norit RB3 for CH₄/N₂ separation using a simplified two-column PSA model. Sensitivity analysis highlighted key process variables affecting performance. Results revealed that ETS-4 and MSC 3K 172 showed greater N₂ selectivity, while Norit RB3 favored CH₄. The outcomes of this study represent a preliminary benchmarking effort, offering a valuable reference framework for the design and optimization of more advanced PSA systems.