



**Carbon Capture from Gaseous Landfill Emissions Part 2: System Design Guidelines for
Carbon Repurposing**

Date of Submission (11/2024)

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Report #2023-03

Acknowledgments

The authors gratefully acknowledge funding from Hinkley Center for Solid and Hazardous Waste Management, Our Technical Awareness Group (TAG) members (Dr. Tim Townsend, John Banks, Travis Barnes, Ron Beladi, Yolanda Daza, Nada Elsayed, Tony Elwell, Dr. Gita Iranipour, Wei Liu, Sam Levin, Linda Monroy, Luke Mulford, Rebecca Rodriguez, Corina Sheridan, Devin Walker, Matt Yung) for the time, inputs and efforts on this project.

ABSTRACT

Landfill gas (LFG) is increasingly used and proposed for a variety of Waste-to-Energy (WTE) technologies either developed or in the process thereof. A challenge for all of these processes is the presence of carbon dioxide (CO_2) and harmful/toxic impurities such as H_2S , ammonia, siloxane, and volatile organic compound in addition to methane (CH_4), the primary energy carrier, and the amounts CO_2 and contaminants tend to increase from aging landfills. Thus, this low energy content and poisonous impurities either hinders the performance of the WTE process (e.g, electricity generation) or necessitates purification for value-added products. The high costs of purification are especially prohibitive for production of renewable natural gas (RNG) for pipeline quality natural gas, due to the stringent requirements. In this work, we applied the polyethylenimine (PEI)-modified polymeric resin adsorbents for CO_2 removal from biogas that were developed in Part I of this project. In the first part of the project funded by the Hinkley Center, amine-immobilized adsorbents were prepared through wet impregnation method and grafting techniques and demonstrated to purify biogas (both surrogate and real LFG) to pipeline/vehicle grades.

In the work reported here, we experimentally tested the CO_2 removal from real landfill gas (Sarasota County, FL) for upgrading into bio-methane (i.e., RNG) via extended stability tests, conducted economic feasibility analysis and environmental impact assessment of a landfill gas upgrading unit. The 50 adsorption-desorption cycle test of the PEI-modified resin (HP2MGL) using real LFG without separation showed $\sim 20\%$ reduction in breakthrough capacity. Post-usage characterization via FTIR indicate degradation/leaching of amine not the amine site blockage due to poisonous impurities responsible for the reduction in capacity. The feasibility analysis showed that pressure drop across the landfill gas upgrading unit is significant (~ 3 bar) due to the particle size of the adsorbent, thereby need compressor compared to blower to pump gas across the system. The need for compression and high regeneration requirement (steam for heat and nitrogen for cooling) accounting for over 50% of total bio-methane production cost of \$123.75 per 1000 m^3 . Taking to account the potential revenue from renewable natural gas sales, governmental carbon tax credit and private companies' carbon credit trading, the landfill fill gas upgrading process could achieve economic viability. In addition, from an environmental perspective, the life cycle of

assessment, sensitivity analysis and the impacts of carbon intensity of the electricity grid mix showed that the use of PEI adsorbents reduce significantly the life cycle GHG emissions in comparison with PSA to produce compressed natural gas (-0.6085 kgCO₂e/kg biogas). When avoided emissions from flaring are considering, the net emissions for the proposed pathway using PEI adsorbents are -55.4 gCO₂e/MJ, showing that LFG-to-CNG using PEI is a promising pathway to reduce the reliance on fossil fuels and reduce GHG emissions. These results leverage previous and ongoing efforts on research and demonstration of LFG to diesel fuel through thermochemical catalytic processes, contaminant removal from LFG, and economic and environmental impact from WTE technologies.

KEYWORDS: Biogas, CO₂ adsorption, PEI adsorbents, LCA, TEA, LFG upgrading

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List of Abbreviations, Acronyms and Units of Measurements

APTES: 3-Aminopropyltriethoxysilane

BET: Brunauer–Emmett–Teller

CNG: Compressed Natural Gas

FTIR: Fourier-Transform Infrared Spectroscopy

GHG: Greenhouse Gas

LCA: Life Cycle Assessment

LFG: Landfill Gas

LNG: Liquefied Natural Gas

MJ: Megajoule

MSW: Municipal Solid Waste

NPCC: Northeast Power Coordinating Council

PEI: Polyethylenimine

PSA: Pressure Swing Adsorption

PV: Photovoltaic

RNG: Renewable Natural Gas

SCFM: Standard Cubic Feet per Minute

SEM: Scanning Electron Microscopy

TSA: Temperature Swing Adsorption

VOC: Volatile Organic Compounds

WTE: Waste-to-Energy

1. INTRODUCTION

1.1. Motivation

The management and utilization of landfill gas (LFG) represents one of the most significant challenges and opportunities in modern waste management and renewable energy production. As organic waste decomposes in landfill environments, it generates a complex mixture of gases that, if not properly managed, contribute substantially to global greenhouse gas emissions[1]. The importance of this issue has grown dramatically in recent years, as landfills now account for approximately 15% of human-related methane emissions globally, making them a critical target for emission reduction strategies[2]. The composition of landfill gas presents unique challenges for utilization and upgrading processes. While methane typically comprises 50-55% of the gas mixture, making it a valuable energy resource, the presence of carbon dioxide (45-50%) significantly reduces its energy content and requires separation for most applications[2, 3]. Furthermore, the gas contains varying amounts of nitrogen, oxygen, and numerous trace compounds including hydrogen sulfide and siloxanes. This complex and variable composition creates substantial challenges for separation technologies, requiring robust and adaptable processing solutions.

Conventional approaches to landfill gas management have evolved significantly over the past decades. The simplest and historically most common approach, flaring, achieves only basic environmental benefits by converting methane to carbon dioxide, typically with an efficiency of around 91.1%[4]. While this reduces the global warming potential of the emissions, it wastes a valuable energy resource. More advanced approaches, such as direct electricity generation, offer improved resource utilization but face challenges related to gas quality and grid integration. For example, while the total electricity generation from landfill gas (LFG) in the United States is ~2.44 GW of installed LFG electricity generation capacity as of 2019[5], which is enough to power more than a million homes, it only accounted for 0.3% of total U.S. electricity generation.

The upgrading of landfill gas to renewable natural gas (RNG) represents a sophisticated and valuable approach to LFG utilization. This process involves removing carbon dioxide and other impurities to produce a high-quality methane product suitable for pipeline injection or vehicle fuel use. The renewable natural gas (RNG) market has experienced remarkable growth over the past decade, particularly in the United States, yet

remains a nascent industry with significant potential for expansion. As of 2024, RNG production represents less than 1% of total natural gas production in the United States, with current production estimated between 0.2 billion to 0.4 billion cubic feet per day (bcf/d) compared to domestic geological gas production of approximately 103 bcf/d [6]. This small but growing market segment presents both unique opportunities and challenges for technological innovation in landfill gas upgrading processes. Especially, With Florida’s population continually increasing (now the third most populous state) and being leading agricultural state (thus generating significant agricultural/organic resources), there is tremendous potential for Florida to be a leader in the conversion of MSW/agricultural residue to energy. However, existing upgrading technologies as in Figure 1 each present significant limitation. Pressure Swing Adsorption (PSA), while well-established, suffers from high methane losses, often reaching 3.5% of total methane content[7]. These losses not only represent a significant economic cost but also contribute to greenhouse gas emissions, partially offsetting the environmental benefits of the upgrading process.

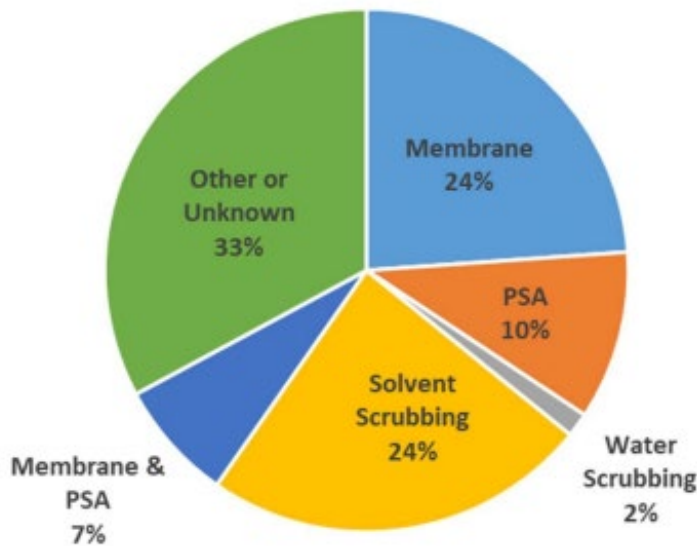


Figure 1: CO₂ removal technologies for U.S. LFG-to-RNG projects in 2018 [1].

Water scrubbing systems, though conceptually simple and chemical-free, require substantial water resources and energy input. The process also struggles with selective CO₂ removal and often requires multiple stages to achieve pipeline-quality gas. Membrane separation technologies offer compact, continuous operation but face challenges with membrane fouling and typically require multiple stages to achieve desired purity levels,

leading to increased complexity and cost. Chemical absorption processes, particularly those using amine solutions, achieve high CO₂ selectivity but face significant challenges with solution degradation and corrosion. The high energy requirements for solvent regeneration also impact the economic viability of these systems. These limitations in existing technologies have driven research toward novel approaches, particularly in advanced materials and process designs. Looking forward, various forecasts project US RNG production to reach between 2 to 4 bcf/d by 2050. According to EPA (Figure 2), there are more than 173 RNG projects were operating in U.S. across 31 states and approximately 40 more were under construction in 2022 [8]. While this represents significant growth from current levels, it would still constitute less than 10% of today's geological gas production. This limited total market potential underscores the importance of developing efficient and cost-effective upgrading technologies.

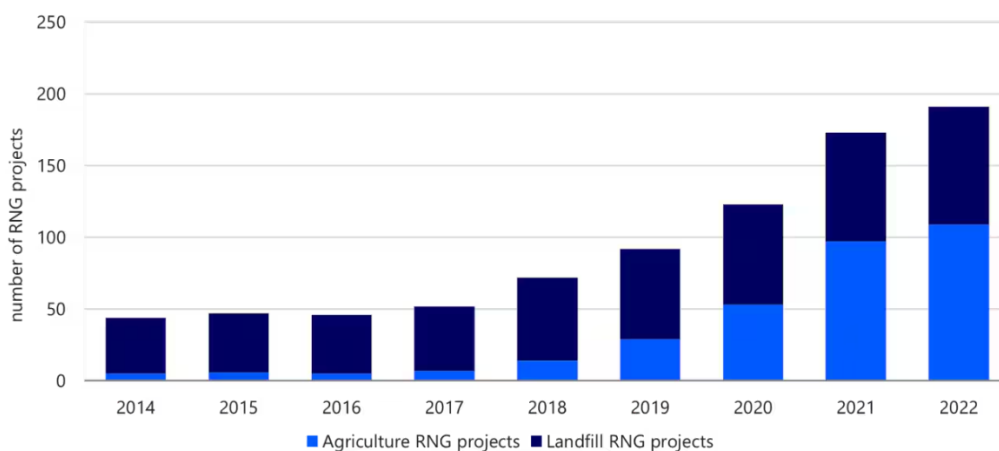


Figure 2: US landfill and agriculture RNG projects in operation, 2014-2022. Source: US Environmental Protection Agency, Rabobank 2024 [6, 8].

The emergence of amine-modified adsorbents represents a promising development in LFG upgrading technology[3, 9-13]. These materials combine the selective CO₂ absorption capabilities of amines with the structural advantages of solid supports. The amine groups provide strong and selective CO₂ binding, while the solid structure eliminates many of the handling and corrosion issues associated with liquid amine systems [3, 14, 15]. Additionally, these materials can operate at moderate temperatures for both adsorption and regeneration, potentially reducing energy requirements compared to conventional techniques.

The technical challenges in LFG upgrading extend beyond simple gas separation and are increasingly shaped by end-user requirements[2, 5, 6, 8]. Pipeline injection standards require high purity levels and consistent quality, while various applications may have specific composition requirements. These demands must be met while maintaining economic viability and minimizing environmental impact, particularly in terms of methane losses and energy consumption. The motivation for this work is the development of a highly efficient, low-cost purification process to enhance the energy content of LFG by removing CO₂.

1.2. Goals and Objectives

The hypothesis guiding the development of this work is that amine functionalized supports will advance CO₂ separations from biogas to increase LFG energy recovery through the efficient and selective adsorption. Some of the key remaining questions are:

1. Is it possible to simultaneously remove water, CO₂ and H₂S?
2. Can better estimates of adsorbent lifetimes be made?
3. What is the environmental impact compared to competing commercial technologies?

Some of the objectives of this work are:

- i) The producible synthesis of two candidate silica supported amine adsorbents, plus characterization and performance testing.
- ii) Updated plant design, environmental impact & economics of CO₂ separation process.
- iii) Enhanced durability testing of top performing material including analysis of real LFG and pressure drop.
- iv) Life cycle assessment (LCA) determining GHG emissions and sensitivity analysis.

1.3. Scope of Work

This work was composed of different steps: First, we synthesized and characterized the best performing amine-functionalized supports from the earlier Part I project. Those two adsorbents were tested for reproducibility and shelf-life in surrogate tests. Once

completed, the top performing material was tested for separation in extended tests with surrogate and real LFG. A detailed characterization of the materials after use was conducted to determine the reason for reduced performance in LFG. The breakthrough times relative to the feed CO₂ molar flow rate were used as a key metric. The stability of the adsorbent was investigated by repeating the adsorption-desorption cycles 50 times.

The experimental results were used to feed techno-economic analyses (TEA) and lifecycle assessments (LCA). The life cycle assessment (LCA) study followed the methodology provided by the International Organization for Standardization (ISO) 1440/14044, which includes (i) goal and scope definition, (ii) the life cycle inventory modeling, (iii) the life cycle impact assessment and (iv) the interpretation phase. Two different functional units were used: 1 kg of biogas and 1 MJ of energy produced. The system boundary used is well-to-pump (WTP), which considers the emissions associated with the production of biomethane, liquefaction or compression of natural gas, transmission and distribution to refueling stations. The sensitivity analysis in this work was conducted to assess the effect of changing (+20 %, + 80%, -20%, and + 80%) the percentage of methane leakage in the Life Cycle GHG emissions comparing two different technologies. In addition, the impacts of Carbon Intensity (CI) of the electricity grid were analyzed in this work after changing the electricity grid for the scenarios analyzed in the LCA.

1.4. Significance of work

The purpose of this effort is to advance strategies for CO₂ removal from biogas and WTE processes and to assess the economic potential and environmental impact of selected technologies. This work proves the performance of high-performing materials in real LFG, including stability, and economic/environmental impact studies to provide the needed results to entice the interest of WTE technologies using landfill gas.

2. BACKGROUND

Landfill gas is a product of the anaerobic digestion of organic component of the municipal solid waste (MSW) and primarily comprised of methane and carbon dioxide along with trace amounts of impurities such as hydrogen sulfide (H_2S), siloxane, ammonia (NH_3), oxygen (O_2) and etc. Currently, the energy content of Landfill gas is either wasted or converted into low-value commodities such as heat and power. However, separation of CO_2 will increase the energy content from ~ 5.5 kWh to 9.67 kWh per m^3 of landfill gas [7](Table 1), where can be used as renewable natural gas either through direct inject into the national natural grid as compressed natural gas (CNG) or liquid natural gas.

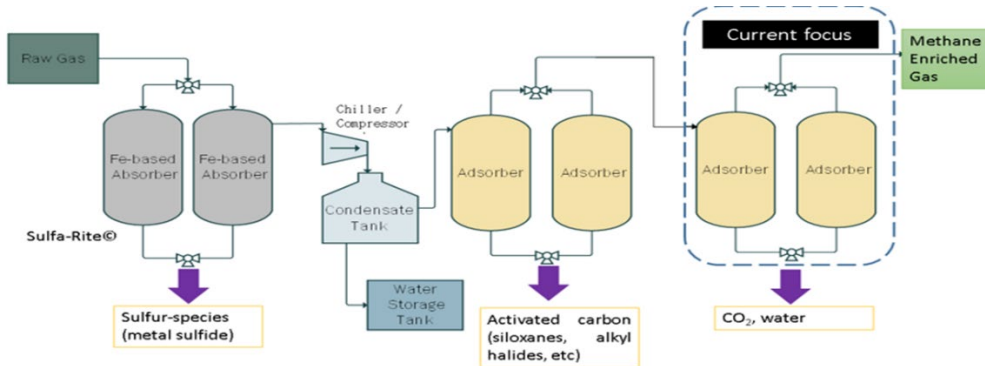


Figure 3: Overall process of LFG clean up.

Typically, harmful and/or toxic compounds, such as H_2S , volatile organic compounds (VOCs), siloxanes, CO, and NH_3 , although present in trace amount are first removed in a landfill gas cleanup process in Figure 3. Iron-based adsorbent such as Sulfa-Rite to remove sulfur containing species and the landfill gas is passed through a chiller to remove water condensates before finally removing other impurities such as siloxanes, alkyl halides with activated carbon. After the landfill gas cleanup, the landfill gas is upgraded into renewable natural gas by separation CO_2 to increase methane concentration to $\sim 95\%$ required for grid injection.

Table 1: Parameter and composition of gases from different sources, impurities, and consequences on upgrading technologies. The United States, California vehicle, and grid inject requirement. [16-19]

Parameter	Unit	Biogas from AD	Landfill Gas	Natural gas	Vehicle and grid injection	Effect of impurity on biogas utilization
Lower heating value	MJ/Nm ³	23	16	40		
	KWh/Nm ³	6.5	4.4	11		
	MJ/Kg	20	12.3	47		
Density	Kg/Nm ³	1.1	1.3	0.84		
Relative density		0.9	1.1	0.63		
Upper Wobbe index	MJ/Nm ³	27	18	55	47.6-56.5	
Methane number		>135	>130	73		
Methane (CH ₄)	Vol %	60-70	35-65	85-92	70-98	
Heavy hydrocarbons	Vol %	0	0	9		
Water vapor (H ₂ O)	Vol %	1-5	1-5			Fouling of engines, compressors, and gas storage tanks due to reaction H ₂ S, NH ₃ , CO ₂ , to form acids.
Carbon dioxide	Vol %	30-40	15-40	0.2-1.5	3	Reduces calorific value and anti-knock properties, and can foul the engine/pipeline.
Nitrogen	Vol %	0-0.5	1.5	0.3-1.0		
Oxygen	Vol %	0	1		<0.2	Susceptible to explosion and corrosion of engines
Hydrogen Sulphide	ppm	0-400	0-100	1.1-5.9	88	Poisoning of the catalytic converter, engine fouling, and health hazards.

						Emissions of SO ₂ , SO ₃
Ammonia (NH ₃)	ppm	100	5	0	<0.0001	Reduces anti-knock fuel properties and causes fouling of engines.
Halide	mg/Nm ³	0-5	20-200		<0.1	Corrosion in engines.
Siloxane	mg/Nm ³		0.82-4	0	0.1	Fouling of engines and catalytic poisoning

A major challenge for conversion of LFG is the low energy content of the LFG compared to natural gas, which is caused by high concentrations of CO₂, which increases as landfills age[5]. As a result, conventional landfill gas upgrading technologies face several significant limitations (Table 2) that hinder their efficiency and economic viability. The processes such as pressure swing adsorption (PSA), chemical scrubbing (CS), organic physical scrubbing (OPS) are notably energy-intensive, requiring substantial power input for operation, while also demanding high operating pressures that increase both safety concerns and equipment costs. Additionally, technologies water scrubbing (WS) typically consumes large volumes of water, raising sustainability concerns and operational expenses. The landfill gas upgrading infrastructure also suffers from corrosion issues in pipelines due to the presence of acidic compounds in the gas stream, leading to increased maintenance requirements and potential system failures. The heavy reliance on compressors, which are essential for gas processing but account for a substantial portion of both capital and operating expenses, creates a significant financial burden that impacts the economic feasibility of these upgrading systems.

Table 2: Limitations of conventional biogas upgrading technologies [16, 17, 20].

CO ₂ Separation Technologies	Limitations
Physical Adsorption	<ol style="list-style-type: none"> 1. High energy and water/solvent demand 2. Prior H₂S and NH₃ separation required

Chemical Scrubbing	<ol style="list-style-type: none"> 1. Relatively expensive 2. High energy consumption 3. Susceptible to corrosion 4. Amine forming and salt precipitation
Pressure Swing Adsorption (PSA)	<ol style="list-style-type: none"> 1. Prior H₂O and H₂S separation required 2. Multi-stage separation required for high purity gas.
Membrane Separation (MS)	<ol style="list-style-type: none"> 1. High methane losses 2. High purity methane-rich gas can be expensive
Cryogenic Separation	<ol style="list-style-type: none"> 1. High energy demand 2. Potential can clog pipeline or heat exchangers

However, due to the potential global warming potential of CO₂, selective adsorbent for its removal from air and flue gas is an emerging topic [21-26]. One of the more promising approaches for CO₂ removal from air is amine functionalized supports [21]. However, there are few studies on amine functionalized supports for removal of CO₂ from methane. In a preliminary series of articles, Belmabkhout et al [27-29] studied amine functionalized silica for CO₂ removal from methane containing streams. The fundamental selectivity for CO₂ adsorption over methane occurs due the amine's basic nature strongly interacting with the acidic CO₂, whereas methane is relatively neutral in terms of acid/base nature due to its high symmetry and lack of free electron pairs. Similarly, Quan et al [30] studied removal of H₂S, also acidic, from biogas using similar materials. Due to the high selectivity and low energy input for regeneration, amine immobilized supports is anticipated to be much more efficient for CO₂ removal from methane in biogas than conventional techniques, which includes CO₂ scrubbing with water [31] and pressure swing adsorption.

In a peer reviewed article from our earlier project [3], we were the first to report that this class of materials (APTES grafted silica) could be used for not only upgrading

using real LFG (containing 68 ppm H₂S), but also potential for simultaneous water removal. This is highlighted in Figure 4. In our mindset, this is a major breakthrough for low pressure CO₂ purification of LFG to RNG, with the results being shown in Figure 4. In these tests, several cycles of adsorption of CO₂ from LFG followed by thermal regeneration are shown. Figure 4(a) shows the CO₂ capacity by cycle, whereas Figure 4(b) shows the water capacity by cycle. The stability for each data set by cycle indicates consistent, stable performance by the adsorbent. In the left most data set (red), The feed is surrogate LFG at 1:1 volume ratio of CH₄:CO₂. The middle data set (blue) indicates a slight drop in uptake when moisture is available, but this is expected and consistent with a separate set of control experiments looking at the effect of water (Figure 5). Both data for Figures 4 and 5 indicate that purification of CO₂ and water can be achieved simultaneously. Our results proved this and it has corroborated by recent articles [32].

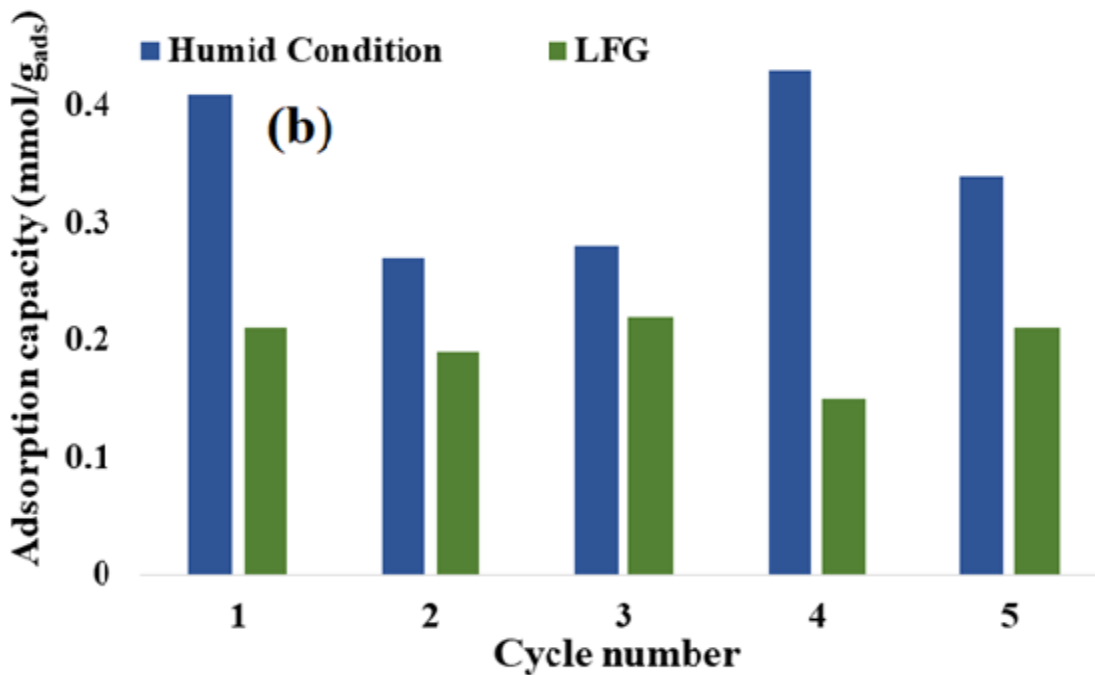
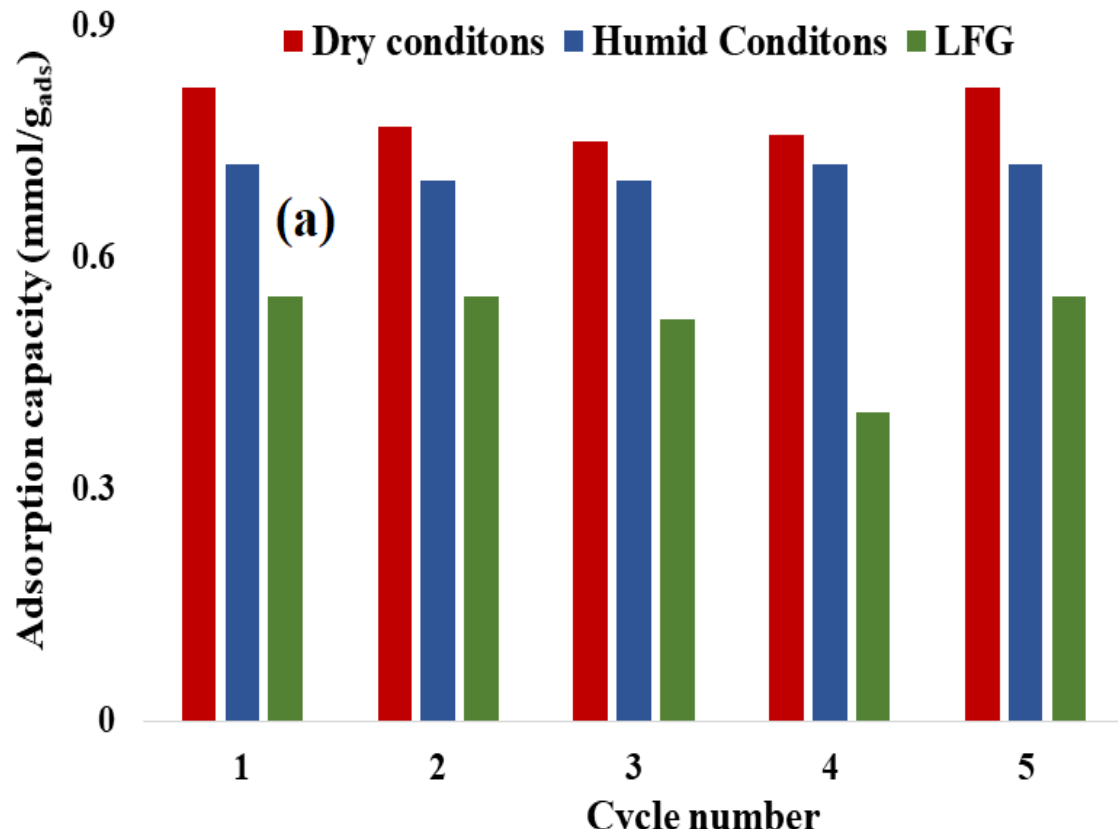


Figure 4: (a) Comparison of CO₂ adsorption capacities with biogas and CO₂/CH₄ in dry and humid (25% RH) conditions as feed. Adsorption at T = 26 °C and desorption at T = 100 °C. (b) Water uptake for the same system. This is the first study that the authors are aware in which real landfill gas was used for tests on CO₂ removal. From our earlier Hinkley project [3].

The right data set (green) is tanked LFG from Sarasota County at 1.4:1 volume ratio of $\text{CH}_4:\text{CO}_2$. Other than nitrogen, the next main component (and the main contaminant concern) was H_2S (68 ppm). There were also minor amounts of alkyl halides and siloxanes (< 10 ppm). These results show that LFG can also be simultaneously purified of CO_2 and water. The role of hydrogen sulfide (H_2S) is not clear currently. This is one goal of the proposed effort. Since both H_2S and CO_2 are acidic gases, it makes sense that there would be competition for basic amine sites. However, we have achieved stable performance for a limited number of cycles. Additional tests, in terms of cycles, and post-use characterization are proposed here to determine how H_2S 's impacts.

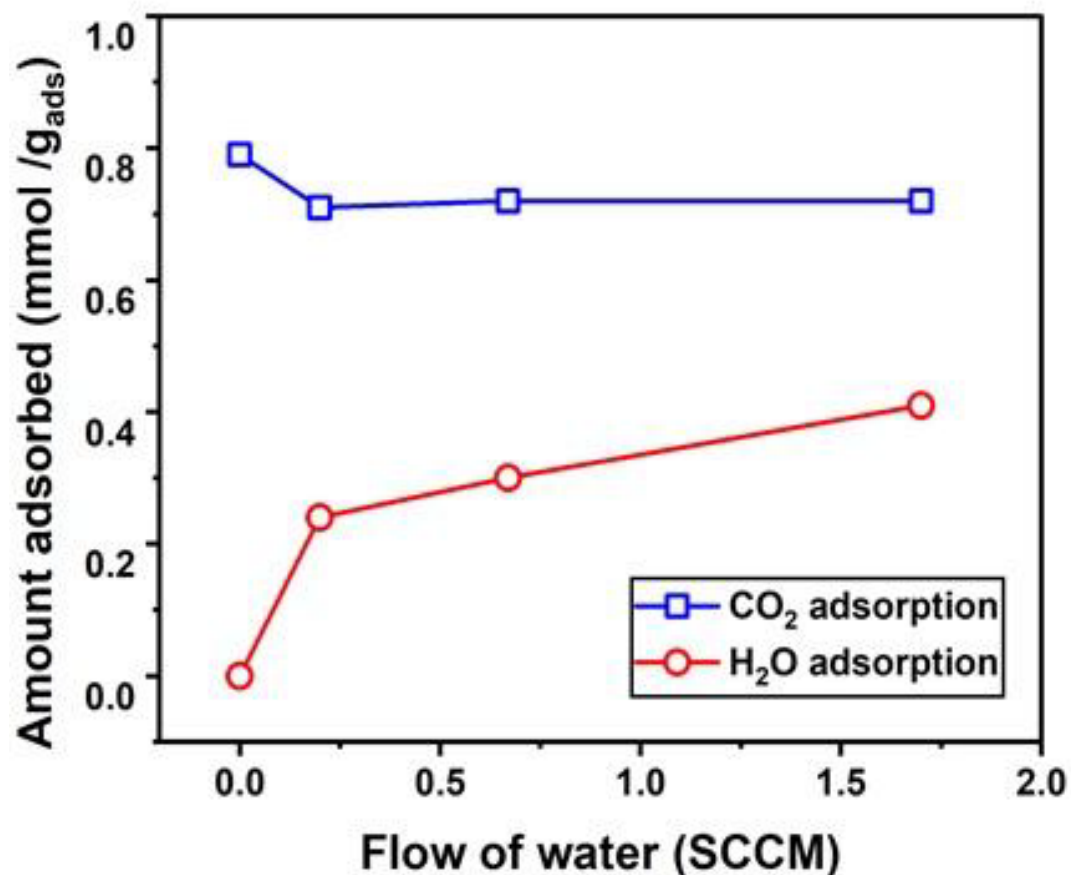
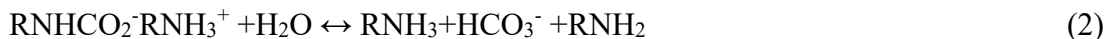


Figure 5: CO_2 adsorption of 26%APTES/SBA-15 in the presence of water in a total feed flow rate of 40 sccm (10 sccm $\text{He}+\text{H}_2\text{O}$, 15 sccm CH_4 and 15 sccm CO_2).

In another peer reviewed article [7], we established a higher performing series of materials (Figure 6) based on the similar chemistry and conducted a preliminary feasibility

analysis. An advantage of the different amine being used is that water is now aiding to increase the uptake rather than hinder it, based on the mechanism our work concluded, as shown in reactions 1 and 2 below.



The enhanced uptake of CO₂ in the presence of steam is demonstrated in Figure 7. Since the fundamental approach is similar to those tested with real LFG, they should also work in a real environment. We hypothesize that the impact of H₂S will also be lessened as it may not be able to become a negative moiety (i.e., carbonate CO₃⁻) equivalent as CO₂ can.

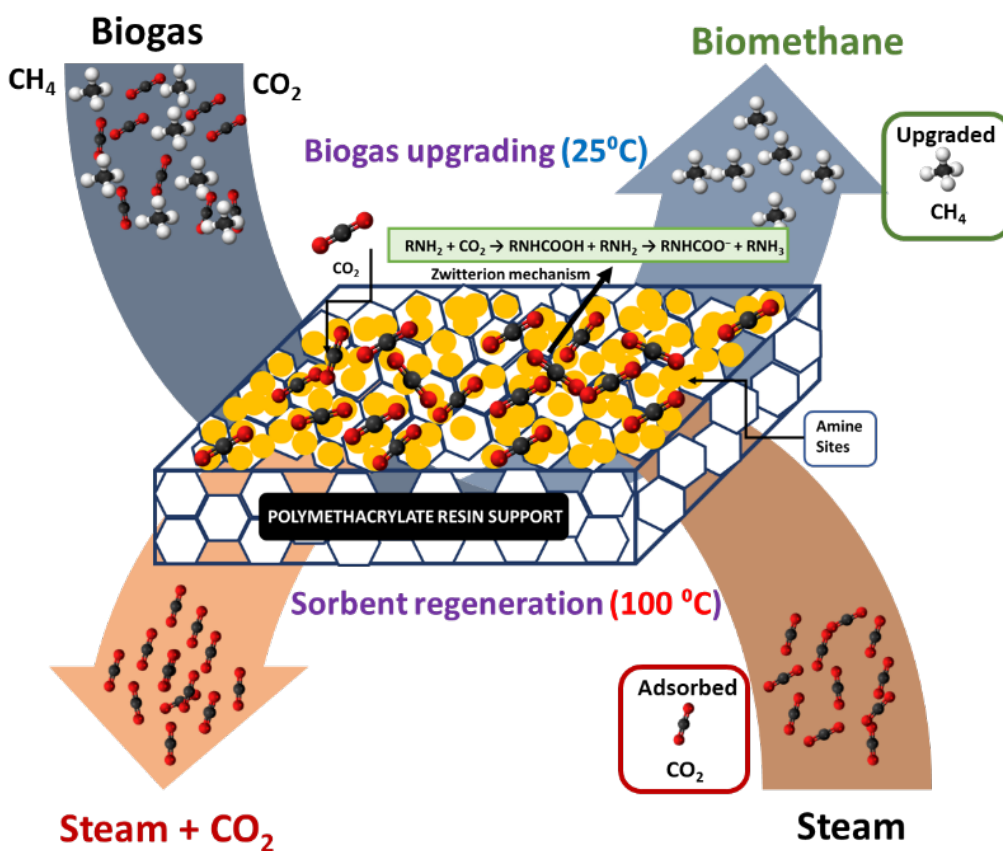


Figure 6: Representation of the contribution and application of our earlier study. From our earlier Hinkley project [7].

The materials PEI/resin materials have ~ 5 times better CO₂ uptake than the APTES/SBA-15 adsorbents used in the first part of the study. We did conduct a feasibility

analysis for the PEI/resin materials [7]. As part of this study (Figure 8), adsorbent costs, lifetime, and capacity (not shown) are major factors. Facility capability is another major factor. We have also compared the results for the supported amine sorbents (SAS) of our lab studies to commercial approaches in Figure 9. In Figure 9, the commercial processes are pressure swing adsorption (PSA), high pressure water scrubbing (HPWS), membrane separations (MS), and chemical scrubbing process (CSP). As noted, the initial feasibility of our results indicates potential to surpass the state-of-technology. As such, it makes sense to complete the R&D to take this SAS is SAS technology to the next stages of design.

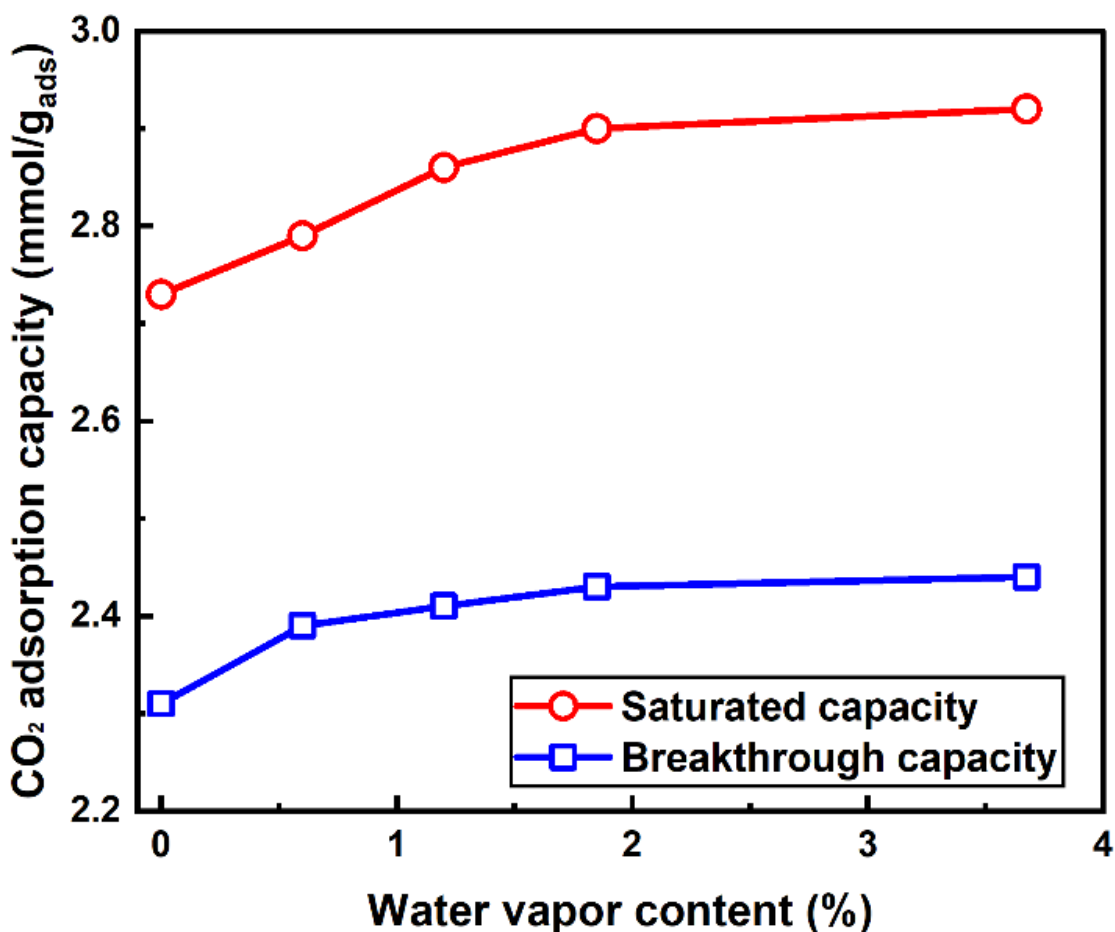


Figure 7: CO₂ adsorption capacity of 30PEI-HP2MGL under various moisture conditions at a total feed flow rate of 40 sccm (10 sccm He/H₂O, 15 sccm CH₄, and 15 sccm CO₂) and adsorption temperature of 25°C [7].

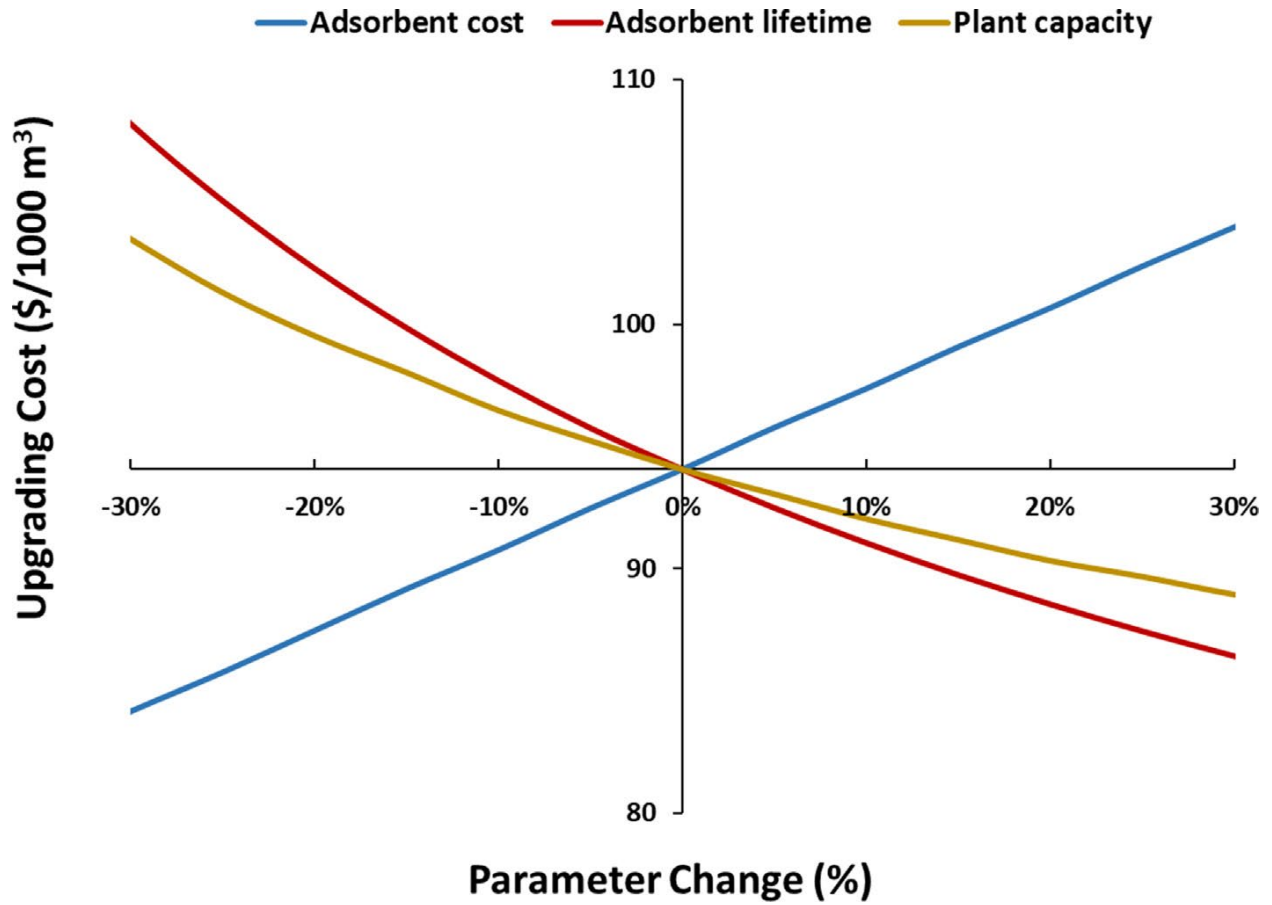


Figure 8: Sensitivity results. The base case is the purchase cost of bulk adsorbent is \$14.12/kg, plant capacity to process 1000 SCFM of raw biogas, and the adsorbent lifetime of 6 months [7].

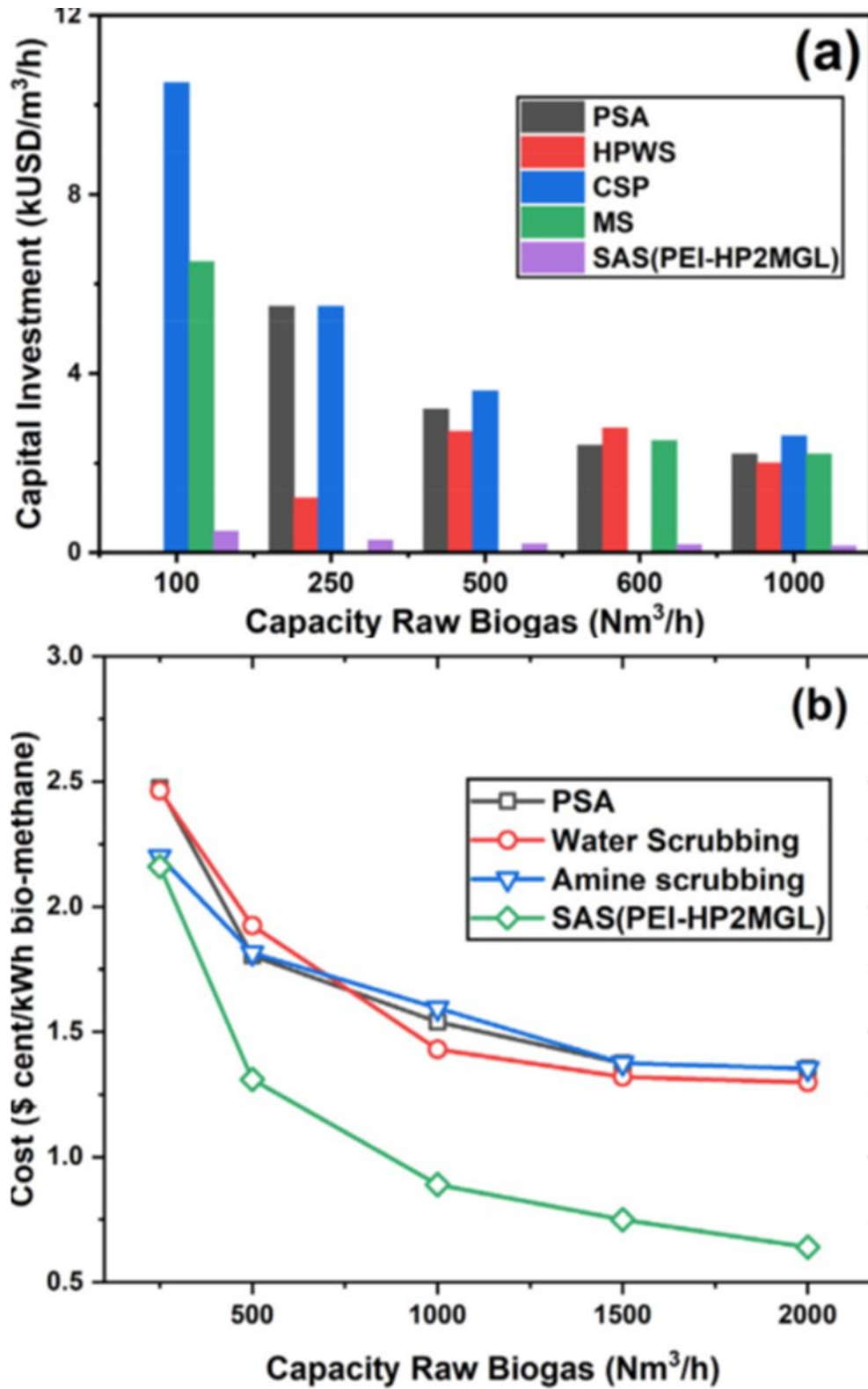


Figure 9: (a) Capital investment cost of different upgrading technologies (non-SAS data [33]); (b) Cost for biogas upgrading for bio-methane (PSA, Water scrubbing, and amine scrubbing data [18]). SAS is Supported amine sorbents (SAS), which is proposed here [7].

There are three major landfill gas (LFG) use pathways that are usual throughout the United States that include: 1) flaring without energy recovery, 2) combustion for electricity generation, and 3) conversion to renewable natural gas (RNG) [33, 34]. There has been a notable increase in the number of studies focused on the Life Cycle Assessment of absorption techniques to assess the environmental impacts and emissions related to the technologies developed, such as membrane and cryogenic separations, pressure swing adsorption, and chemical scrubbing, among others [35]. Upgrading technologies to landfill gas has various advantages, such as the reduction of the dependence on natural gas (through the development of another source of methane), and the environmental impacts that can be reduced by offering a renewable source of energy, fuels, and chemicals production [36].

Several studies examined the life-cycle impacts of different LFG management pathways on the environment and carbon capture processes, as can be seen in Table 3.

Table 3: Literature review on LCA studies for carbon capture technologies.

Reference	Scenarios studied	Functional unit
[33]	1) Flare the LFG (diesel to power the tractor-trailers); 2) Generate electricity from the LFG (diesel to power the tractor-trailers); 3) Refine the LFG to RNG and use to power CNG tractor-trailers; 4) Generate electricity from the LFG and use to power electric tractor-trailers.	Total net annual emissions (in kg/year) of each type of pollutant generated (CO ₂ was the major pollutant of interest).
[37]	1) The current MSW management system in the central district of Tianjin; 2) LFG utilization to produce electricity; 3) Incineration; 4) Materials recycling; 5) Centralized composting; 6) Anaerobic digestion; 7) Integrated system.	Disposal of the MSW collected by the central districts of Tianjin city in 2006 (909,160 tons).
[38]	Life cycle emissions of post-combustion CO ₂ capture technologies based on membrane separation and amine absorption processes.	Capture of 1 tonne of CO ₂ .
[39]	1) Conventional solvent absorption process with monoethanolamine (MEA); 2) The UNO MK 3	Capture of 1 tonne of CO ₂ .

	process with potassium carbonate absorbent and stainless-steel absorption and regeneration columns; 3) The UNO MK 3 process with potassium carbonate absorbent and concrete absorption and regeneration columns.	
[40]	1) Landfilling; 2) Biogas burned to produce electricity; 3) a combination of incineration and anaerobic digestion; 4) gasification and anaerobic digestion; 5) incineration; 6) direct gasification.	1 tonne of solid waste treated.
[41]	1) Landfilling without any further treatment; 2) biogas treated and burnt to produce electricity, biogas (from anaerobic digestion) and compost are produced; 4) incineration to produce electricity.	The amount of waste produced in 2003 by the city of Rome.
[42]	Power generation of five pulverized coal-based steam power plants, which differ in the year of installation, the conversion efficiency, and in the ability and efficiency to capture CO ₂ (MEA).	1 kWh net electricity produced
[43]	Municipal solid waste incineration (MSWI) with and without carbon capture and storage (CCS) via MEA.	1 tonne of wet MSW as received at the incinerator.
[44]	Municipal solid waste (MSW) grate incineration power plants: 1) without CO ₂ capture; 2) with CO ₂ capture including (MEA) absorption; 3) pressure/vacuum swing adsorption (P/VSA), and 4) oxy-fuel combustion (Oxy).	1 tonne of MSW
[45]	1) Post-combustion CO ₂ recovery through chemical absorption with MEA; 2) alternative post-combustion technologies (membrane separation, cryogenic, PSA); 3) pre-combustion	1 kWh of net electricity produced

CO₂ recovery with Selexol; 4) oxy-fuel
technology.

3. METHODS

3.1. Experimental Methods

3.1.1. Material Synthesis

Branched polyethyleneimine (MW=600, 99%) was obtained from Sigma-Aldrich and used as the amine source. Commercial adsorbent resin, HP2MGL, bought from Alfa Aesar was the polymeric resin support. The amine modified resin adsorbent was synthesized through wet impregnation method, following the procedure discussed in previous work[7]. 5g of PEI were added to 30 mL of methanol and stirred at for 30 mins (250 rpm and 40 °C). The resin was first dried at 80 °C for 1h before added to the homogeneous PEI and methanol solution and continued stirring at 40 °C to remove methanol and dried at 80 °C for 12h.

3.1.2. LFG Upgrading Performance Testing

The landfill gas used in this experiment was sourced from the Sarasota (Florida) county municipal solid waste (MSW) landfill site with the composition listed below in Table 4. To study the potential simultaneous separation of H₂S and CO₂ and the impact of other impurities on the stability of the PEI-modified Resin, there was no pretreatment of LFG obtained from our landfill site.

Table 4: Composition of biogas used in this study [3, 47].

Compound	Mole percent on dry basis (%)^{a,b}
CH ₄	56.7
CO ₂	40.5
N ₂	2.4
O ₂	0.4
H ₂ S	68 (ppm)
CO	6 (ppm)
Siloxanes	4 (ppm)
Halides	3 (ppm)

a – Unless stated otherwise

b – LFG is water-saturated

The landfill gas upgrading experiments were performed in a 6.35 mm fixed bed set-up with a stainless-steel reactor and the adsorbent (1g) loaded between 2 glass wool layers. For breakthrough experiment, there are two independent feed lines. The first one contains a mixture of LFG (41.4 sccm) and a tracer (Ar=5 sccm) and while is second one is a purely helium (46.4 sccm) gas. Two-back pressure regulator (Swagelok) was used to maintain the feed line under similar pressure and a 2-position 4-way Valco manual valve was used to switch between the landfill gas and the purge gas stream. The flow of stream out of the reactor is monitored with an online MKS Cirrus mass spectrometer. The CO₂ breakthrough adsorption capacity was estimated as the concentration of CO₂ captured until the first detection of CO₂ in the exit flow. The adsorption experiment was performed at 30 °C under feed 1 until the bed is saturated with CO₂ and the valve is switched to Feed 2 and kept for 30 mins before the bed is heated to 100 °C (5°C/min) and kept for 1 hour to completely regenerate the adsorbent bed.

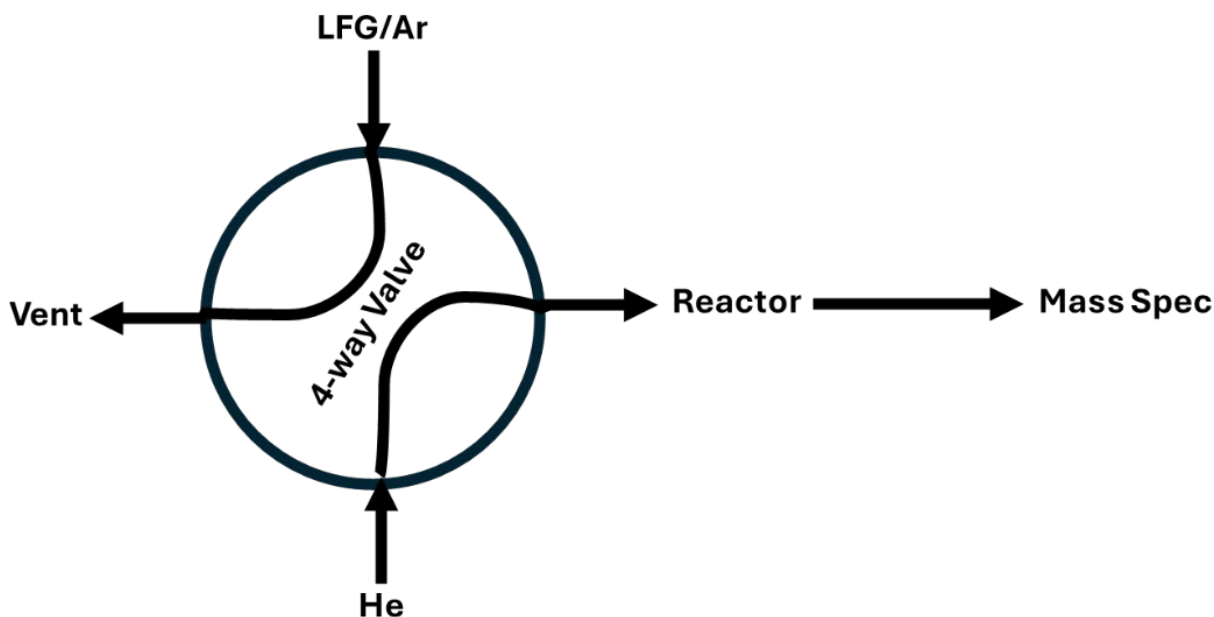


Figure 10: Process Flow Diagram of LFG Upgrading Experimental Set up.

3.1.3. Material Characterization

Nitrogen physisorption and static CO₂ adsorption measurements were conducted on a Quantachrome Autosorb-iQ. The BET (Brunauer–Emmett–Teller) method assessed the surface area, pore volume, and pore size distribution of the synthesized adsorbents. Approximately 0.1 g

of the sample was degassed under vacuum at 100°C for 5 hr prior to analysis. The adsorption-desorption isotherms were then recorded at 77K for N₂ physisorption to determine the surface area and pore characteristics of the materials. For static CO₂ chemisorption, ~50 mg of samples were outgassed at the condition as above and CO₂ uptake capacity measurement performed at 298.15K.

FTIR analysis was performed to identify the functional groups present in the adsorbents and monitor any changes following exposure to operational conditions. FTIR spectra were recorded using a Thermo Scientific Nicolet IS50 instrument in the range of 4000–400 cm⁻¹ with a resolution of 4 cm⁻¹, focusing on identifying characteristic peaks associated with amine functionalization and polymeric structures.

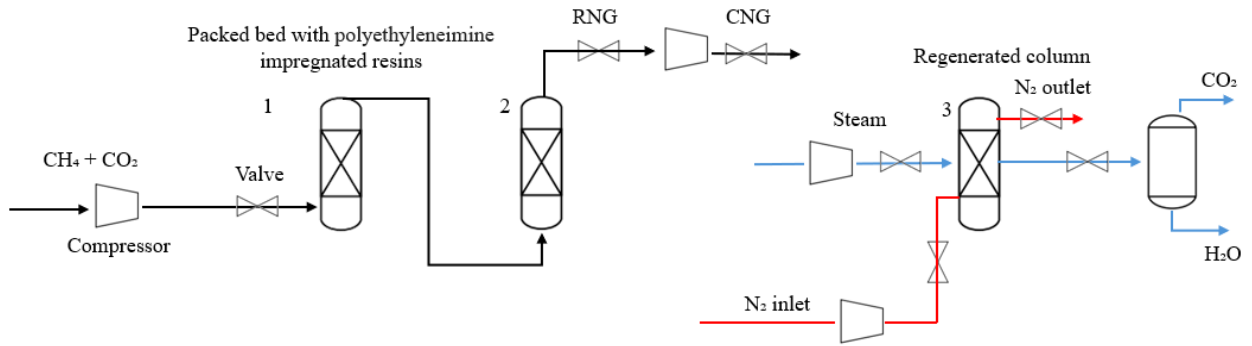
Scanning electron microscopy (SEM) was used to observe the morphology of the synthesized adsorbents. Samples were mounted on double layer of carbon and copper tape to enhance conductivity. Imaging was performed on a Hitachi SU70 SEM at an accelerating voltage of 5-10 kV, with both low- and high-magnification images taken to examine the particle shape, size distribution, and surface features of the material.

3.2. Technoeconomic Analysis

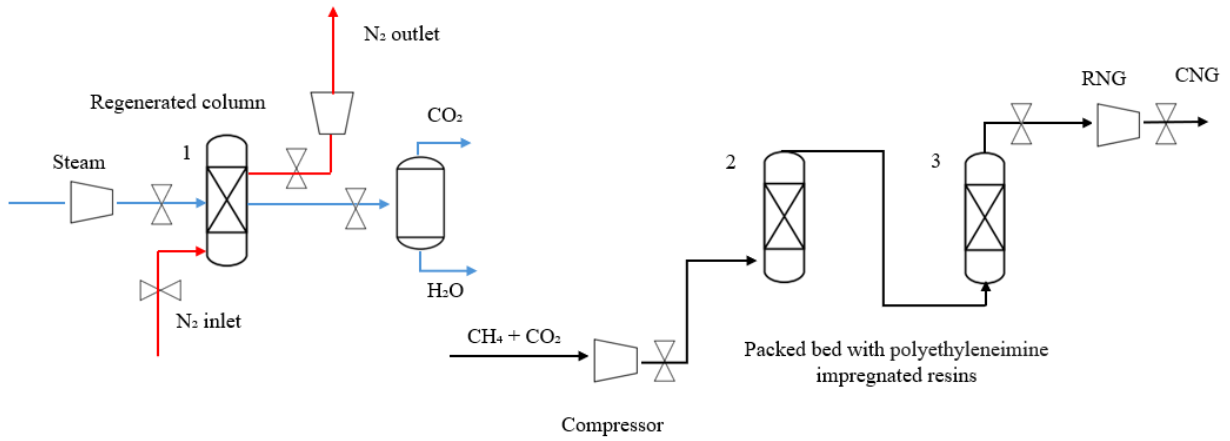
3.2.1 Temperature Swing Adsorption Process Flow

In this study, the composition of biogas is modeled as 56.7 % methane, 40.5 % carbon dioxide [7] as major constituents and it is used as the only feedstock for this process. The adsorption the CO₂ from biogas using amine functionalized supports proposed in this project is represented in the process flow diagram (PFD) reported in Figure 11. Three bed systems (leg-lead for two of them and one in regeneration) are used. Figure 11a represents the first regeneration mode in which the first two bed systems will be used in the process while the third one will be regenerated with N₂ flow (cooling step) and steam (flash vessel for separation of CO₂ and water). Figure 11b and c are also modes of operation of the system.

a)



b)



c)

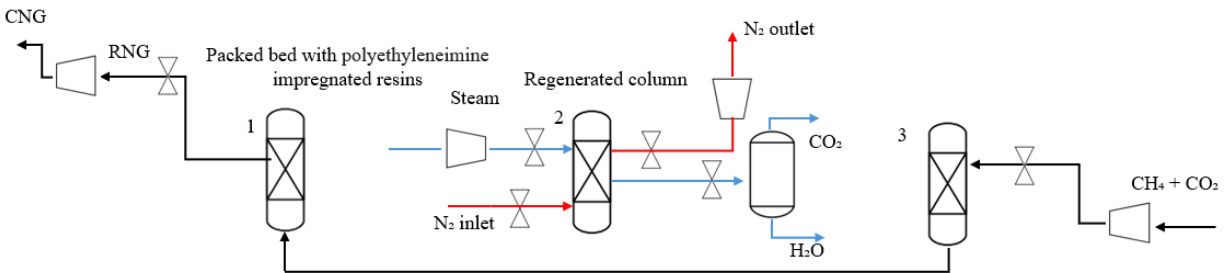


Figure 11: (a) First regeneration mode for the system using two beds, (b) second regeneration mode and (c) third regeneration mode.

3.2.2. Pressure Drop Estimation

The pressure drop along the length of the packed adsorbent bed is estimated using the Ergun Equation[46] shown in equation 1 below;

$$\Delta P = \frac{150(1 - \emptyset)^2 \mu v}{\emptyset^2 D_p^2} L + \frac{1.75(1 - \emptyset) \rho v^2}{\emptyset^3 D_p} L \dots\dots\dots \text{Equation 1}$$

Where,

ΔP = Pressure drop (Pa)

\emptyset = Adsorbent bed void

μ = Dynamic Fluid Viscosity (Pa.s)

v = Fluid velocity (m/s)

D_p = Particle diameter (m)

L = Packed bad length (m)

ρ = Biogas density (kg/m³)

3.2.3 Economic Analysis

The fixed-bed temperature swing adsorption system as illustrated in the process flow diagram was used for the economic analysis. The process cost and energy requirements were estimated similarly to our previous work[7] with the additional of a N₂ cooling system.

The energy requirement calculation was performed in moles of CO₂.

$$1 \text{ mole of CO}_2 \text{ adsorbed} = \frac{R.F_{CH4} * P.F * MW_{CH4}}{R.F_{CO2} * MW_{CO2}} = n_{CH4} \dots\dots\dots \text{Equation 2}$$

Where P.F = Purity factor based on the requirement for pipeline gride and R.F = Ratio of CO₂ in the inlet raw biogas.

Blower operating cost C₁:

The operating cost of the blower is the product of the energy required for the blower and the cost of electricity; C_E (\$/Joule) and it is given as;

$$C_1 (\$/tonnes) = \Delta P (Pa) * Q_{inlet}(m^3/hr) * t_a(hr) * C_E / (n_t * n_{CH4}) \dots\dots\dots \text{Equation 3}$$

Where n_t = Tons of CO₂ separated = 22730 moles of CO₂

Regeneration cycle operating cost C₂:

$$C_2 (\$/ton) = C_s((m_{ads} * C_{pads} * \Delta T_{ads}/n_{CO2}) + (m_{wall} * C_{pwall} * \Delta T_{wall}/n_{CO2})) + (\Delta H) / (n_t * n_{CH4}) \dots\dots\dots \text{Equation 4}$$

Where C_s = Cost of 1 GJ of low-grade steam

Vessel Capital Cost C₃:

The base cost of the process vessel, C_p , is given as;

$$C_p = \text{Antilog}_{10}(3.4974 + 0.4485 \log_{10} V + 0.1074(\log_{10} V)^2) [47] \dots\dots\dots \text{Equation 5}$$

Where V = volume of the process vessel required.

The volume requirement of the process vessel is calculated as;

$$V = (1 + B_v) * (m_{ads} / \rho_{ads}) \dots\dots\dots \text{Equation 6}$$

B_v = Void ratio of the adsorbent bed

m_{ads} = Mass of adsorbent required

ρ_{ads} = Density of adsorbent

The vessel pressure factor is given as

$$F_{p,vessel} = \text{Pressure factor} = \frac{\frac{(P+1)D}{2(850-0.6(P+1))} + 0.00315}{0.0063} [47] \dots\dots\dots \text{Equation 7}$$

Where D = diameter of the vessel in meters, and P = Operating pressure (barg)

Material Factor and Bare module

The bare module cost of the vessel includes the buying cost, and the installation cost is given by;

$$C_{bm} = \text{Bare Module cost} = C_p F_{bm} = C_p (2.25 + 1.82 F_m F_p) [47] \dots\dots\dots \text{Equation 8}$$

(S4.7)

The Bare module cost is adjusted by interest rate to give the present cost of the vessel.

$$C_v = C_{bm} * (1 + i)^{13} \dots\dots\dots \text{Equation 9}$$

$$C_3 = \text{Annualized Vessel Cost (\$/ton)} = \frac{C_v * t_{cycle}}{N_t * N_{yr} * t_{yr} * n_{CH4}} \dots\dots\dots \text{Equation 10}$$

Where t_{cycle} = Time to complete a TSA cycle (hr)

N_{yr} = The lifetime of the process vessel (yr)

t_{yr} = The number of hours in a year

Adsorbent Capital Cost C4 :

The annualized capital cost of adsorbent, C_4 (\$/tons), is given as

$$C_4 = \text{Annualized adsorbent cost (\$/ton)} = m_{ads} \frac{C_{ads} * t_{cycle}}{N_t * N_{yr} * t_{yr} * n_{CH4}} \dots\dots\dots \text{Equation 11}$$

Where m_{ads} is the mass of adsorbent required per vessel (in kg), C_{ads} is the cost of buying one kg of adsorbent, t_{yr} is the number of hours in a year, N_{yr} is the lifetime of the adsorbent, t_{cycle} is the time to complete a TSA cycle in hours.

To the best of our knowledge, presently the adsorbent is not commercially available yet and information on the cost incurred in the purchasing of 30PEI-HP2MGL in bulk is unavailable. The cost coefficient (C_{ads}) was calculated using the cost of the individual raw materials required for the synthesis of the adsorbent. We assumed that the cost of synthesis contributes to around 33% of the overall cost for buying the adsorbents in bulk. Therefore, the synthesis cost was multiplied by 3 to estimate the overall cost including the raw materials, synthesis, labor, maintenance, and utility cost required for the bulk production of the adsorbent.

The cost of raw materials (obtained from Alibaba websites[48])

1. HP2MGL = \$5.34 per kg
2. PEI = \$4 per kg

Blower Capital Cost C5 :

$$C_p = \text{Capital cost} = \text{Antilog}_{10}(2.2891 + 1.3604 \log_{10} P - 0.1027(\log_{10} P)^2) \dots \text{Equation 12}$$

Where P is the fluid power

The bare module cost of the blowers included the purchase and installation cost=

$$C_{BM} = F_{BM} * F_M * C_p \dots \text{Equation 13}$$

The bare module cost is then adjusted by interest rate and given as C_B,

$$C_B = C_{BM}(1+i)^{13} \dots \text{Equation 14}$$

$$C_5 = \frac{C_b * t_{cycle}}{N_t * N_{yr} * t_{yr} * n_{CH4}} \dots \text{Equation 15}$$

Cost of operating labor C₆:

We assumed that 4.5 operators are hired for each operation needed in the plant at any time and the plant and system operator wage C_{ol} (\$/hr).

The number of operators required for the process per shift, N_{ol} is given by;

$$N_{ol} = (6.29 + 31.7P^2 + 0.23N_{op})^{0.25} [47] \dots \text{Equation 16}$$

Where, P = Number of processing steps involving the handling of particulate solids

N_{op}= Number of non-particulate processing steps

In this case study, there are no particulate solids processing units, and only the adsorber is considered for non-particulate processing equipment.

$$\text{Cost of operating labor } C_6 (\$/\text{ton}) = \frac{4.5 * N_{ol} * C_{ol} * N_w * NN_{hr}}{N_t * n_{CO2}} \dots \text{Equation 17}$$

Cost of waste disposal C₇:

$$C_7 = m_{ads} \frac{C_t}{N_t * N_{yr} * n_{CH4}} \dots \text{Equation 18}$$

Where m_{ads} is the mass of adsorbent required per vessel (in Kg), C_t is the cost of disposing one kg of adsorbent, N_{yr} is the lifetime of the adsorbent.

Cost of Cooling Adsorbent Bed C₈:

$$\text{Heat Load (Q)} = m * C_{p_{ads}} * \Delta T_{ads} \dots \text{Equation 19}$$

Required Cooling Capacity = Heat Load (Q)/Cooling time per cycle

$$N_2 \text{ volumetric flow rate} = \text{Cooling capacity} / (C_{pN_2} * \Delta T_{N_2} * \rho_{N_2}) \dots\dots\dots \text{Equation 20}$$

$$C_8 = \text{Cost per volume} * V_{N_2} \text{ per cycle} * \text{cycles per day} * \text{Operational day}$$

We assume N₂ cost = 40 cent per m³ based on Nitrogen gas vendor[49]

3.3. Life Cycle Assessment (LCA)

3.3.1. Goal and Scope definition

The goal of this LCA was to compare the greenhouse gas emissions (GHG) of capturing CO₂ from landfill gas using PEI adsorbents with different technologies and end products. The results presented in this work were calculated using the R&D GREET.Net (The Greenhouse gases, Regulated Emissions, and Energy use in Technologies Model - 2023). Two different functional units were used: 1 MJ of energy produced (useful to compare GHG of different end products), and 1 kg of biogas (used to compare different pathways/technologies of LFG upgrading). The system boundary used is well-to-pump, which considers the emissions associated with the production of biomethane, liquefaction or compression of natural gas, transmission and distribution to refueling stations. Figure 12 represents all the four scenarios analyzed using this system boundary.

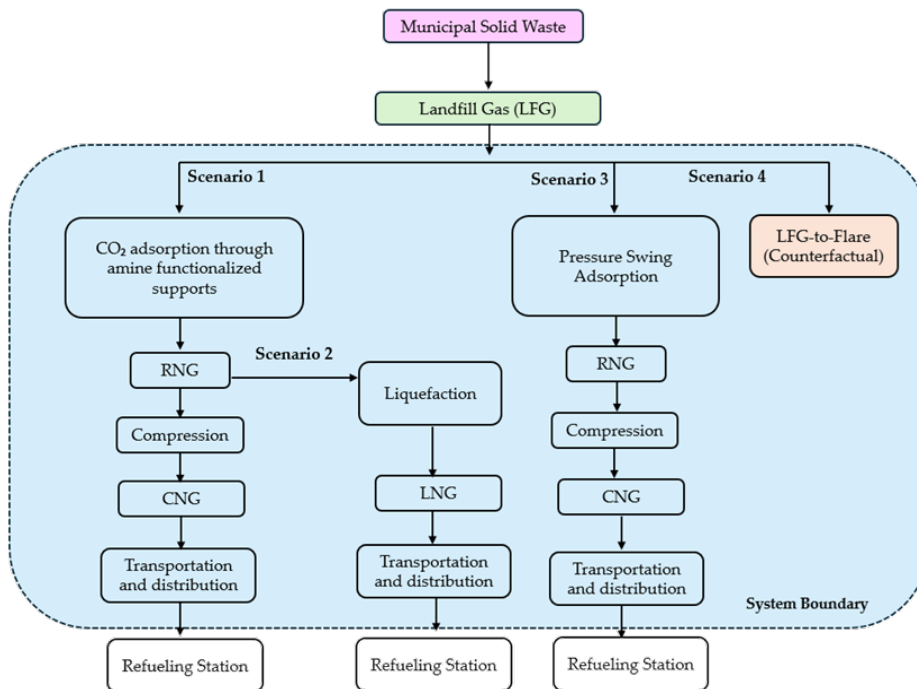


Figure 12: System Boundaries – Well-to-Pump scenarios.

3.3.2. Major inventory Data

Table 5 shows a description of the major inventory data used in the LCA analysis. As can be seen, the flaring efficiency was considered 91.1 % [4], and the biogas leakage during biogas upgrading was based on literature results, as seen in Table 5. In addition, the distance until the refueling station, used as an assumption for this work, is five miles, and boil-off losses related to the liquified natural gas storage and transportation were considered equal to six percent [50].

Table 5: LCA major inventory data.

Assumptions	Value	Unit	Reference
Biogas			
Flow rate	15017137	m ³ /year	
CH ₄ content	56.7	% (mole percent – dry basis)	
CO ₂ content	40.5	% (mole percent – dry basis)	
Flaring			
Flaring efficiency	91.1	%	[1]
Biogas upgrading - CH₄ leakage			
Pressure Swing Adsorption	3.5	%	[51]
Amine adsorbents	0.07	%	[52]
Energy requirements			
Compression	0.016	MJe/MJ feed	[53]
Liquefaction	0.043	MJe/MJ feed	[53]
Transportation			
CH ₄ leakage	0.08	g CH ₄ /MMBtu-mile	[54]

3.3.3. Sensitivity Analysis and Impacts of Carbon Intensity of the electricity grid

The influence of important parameters involved in a process, or a pathway can be analyzed through a sensitivity analysis [55]. The sensitivity analysis in this work was conducted to assess the effect of changing (+20 %, + 80%, -20%, and + 80%) the percentage of methane leakage in the Life Cycle GHG emissions comparing two technologies (Pressure Swing Adsorption, and the use of amine adsorbents proposed in this work).

The impacts of Carbon Intensity of the electricity grid were analyzed in this work after changing the electricity grid for scenarios 1 and 3 (SC1 and SC3, using PEI adsorbents and PSA, respectively) and analyzing the impacts of in the reduction in GHG emissions when considering the credits for avoiding flaring. The grid mixes used for this comparison were: NPCC (Northeast Power Coordinating Council), FRCC (Florida Reliability Coordinating Council), ASCC (Alaska Systems Coordinating Council), U.S. Mix, and Solar (Electricity derived from grid-connected PV + battery system).

4. RESULTS & DISCUSSION

4.1. Experimental Results

The synthesized PEI-HP2MGL sample were characterized and compared to the original sample in our previous publication to confirm reproducibility. N_2 physisorption was used to probe the surface area and pore volume. As shown in Figure 13, the PEI-HP2MGL tracked the type II adsorption-desorption isotherm, which is typical of microporous nature of the support material. The synthesized adsorbent showed a significant drop in the surface area from 587 (in pristine HP2MGL) to 27 m^2/g (PEI-HP2MGL) due to amine functionalization (Table 6) and this is similar to the originally synthesized material. The trend was also observed with pore volume, indicating the presence of amine and that synthesized material is reproducible.

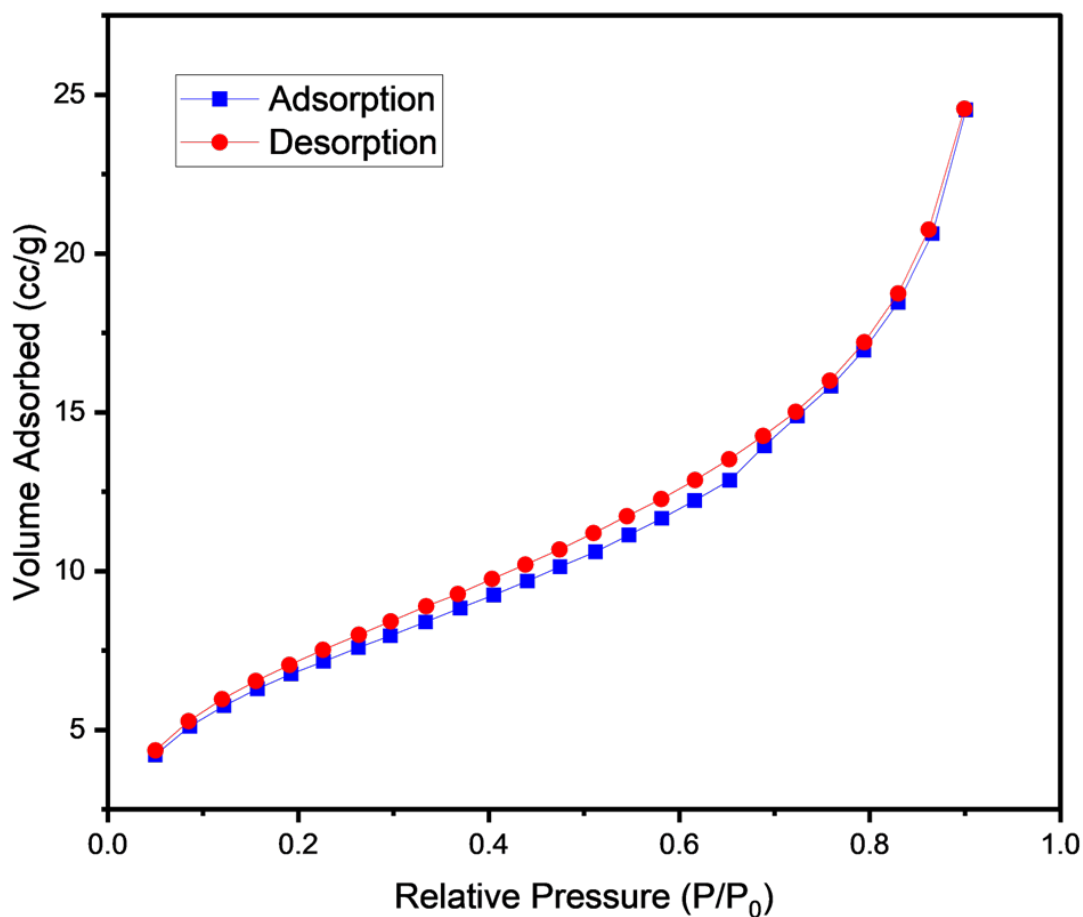


Figure 13: N_2 adsorption-desorption isotherm of reproduced PEI-HP2MGL.

Table 6: Textural properties of original and reproduced PEI-HP2MGL.

Samples	Surface Area (m ² /g)	Pore Volume (cm ³ /g)
HP2MGL	587	1.45
PEI-HP2MGL_O	28	0.62
PEI-HP2MGL_R	27	0.3

The static CO₂ adsorption-desorption isotherm of the reproduced and the original adsorbent were performed and compared to confirmed CO₂ adsorption capacity of the PEI-HP2MGL adsorbent. As shown in Figure 14 the CO₂ sorption isotherm is very similar in hysteresis and shape, indicating that mode of adsorption is the same. Additionally, the difference of 0.2 mmol_{CO2}/g_{ads} in the CO₂ uptake capacity between the two sample indicate performance reproducibility as well.

In a simulated biogas gas stream of CH₄/CO₂/inert at 40/40/20 vol%, and the result is shown in Figure 15. The breakthrough capacity was 2.1 mmol_{CO2}/g_{ads} with saturated capacity of 2.3 mmol_{CO2}/g_{ads} and a breakthrough time of 150s on 1g of adsorbent as shown in Figure 15b. This performance is also consistent with already published work on this topic, confirming the reproducibility of the amine-modified polymeric resin.

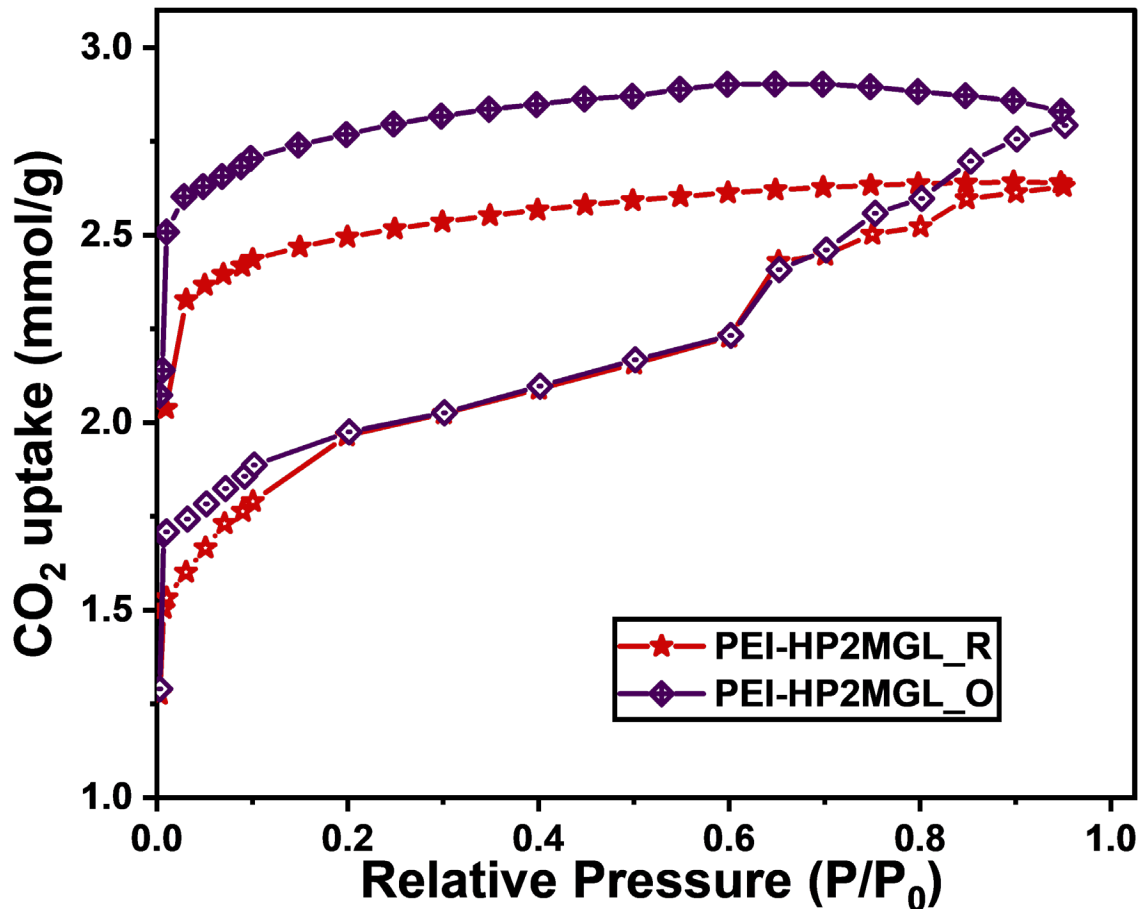


Figure 14: Static CO₂ isotherm of original and reproduced PEI-HP2MGL.

The experimental investigation using real landfill gas from Sarasota County demonstrated the robust performance of PEI-modified adsorbents under actual operating conditions. The landfill gas composition consisted of approximately 56% methane, 40.5% CO₂, with significant impurities including hydrogen sulfide (60 ppm), nitrogen, siloxanes, and other trace contaminants. This complex mixture provided a rigorous test of the adsorbent's selectivity and stability.

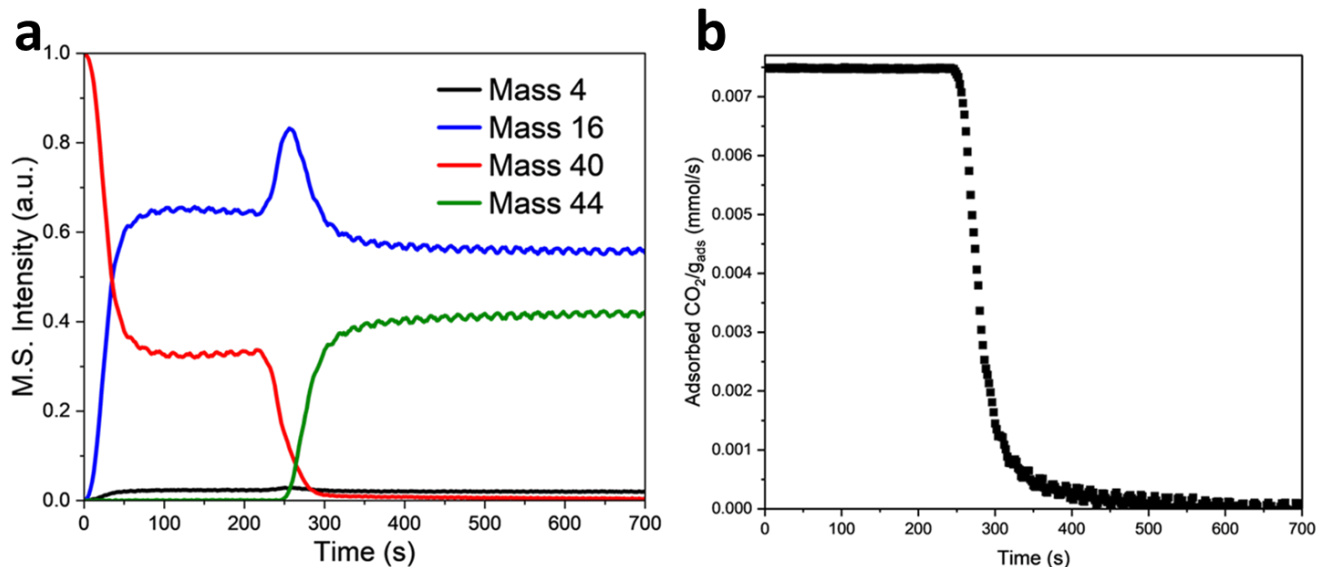


Figure 15: (a) CO₂ separation from simulated biogas (b) CO₂ breakthrough curve of PEI-HP2MGL.

As shown in Figure 16, through over 50 consecutive adsorption-desorption cycles, the material demonstrated consistent CO₂ separation capability, though with some notable performance changes. The breakthrough capacity showed a gradual decline, ultimately resulting in a ~20% reduction from initial performance by the 50th cycle. Importantly, the saturated capacity remained approximately 30% higher than the breakthrough capacity throughout the testing period, indicating maintenance of the material's fundamental adsorption properties despite some degradation in kinetic performance. These results indicate that optimization of adsorbent amount, cycle time, and regeneration are important and could be further examined.

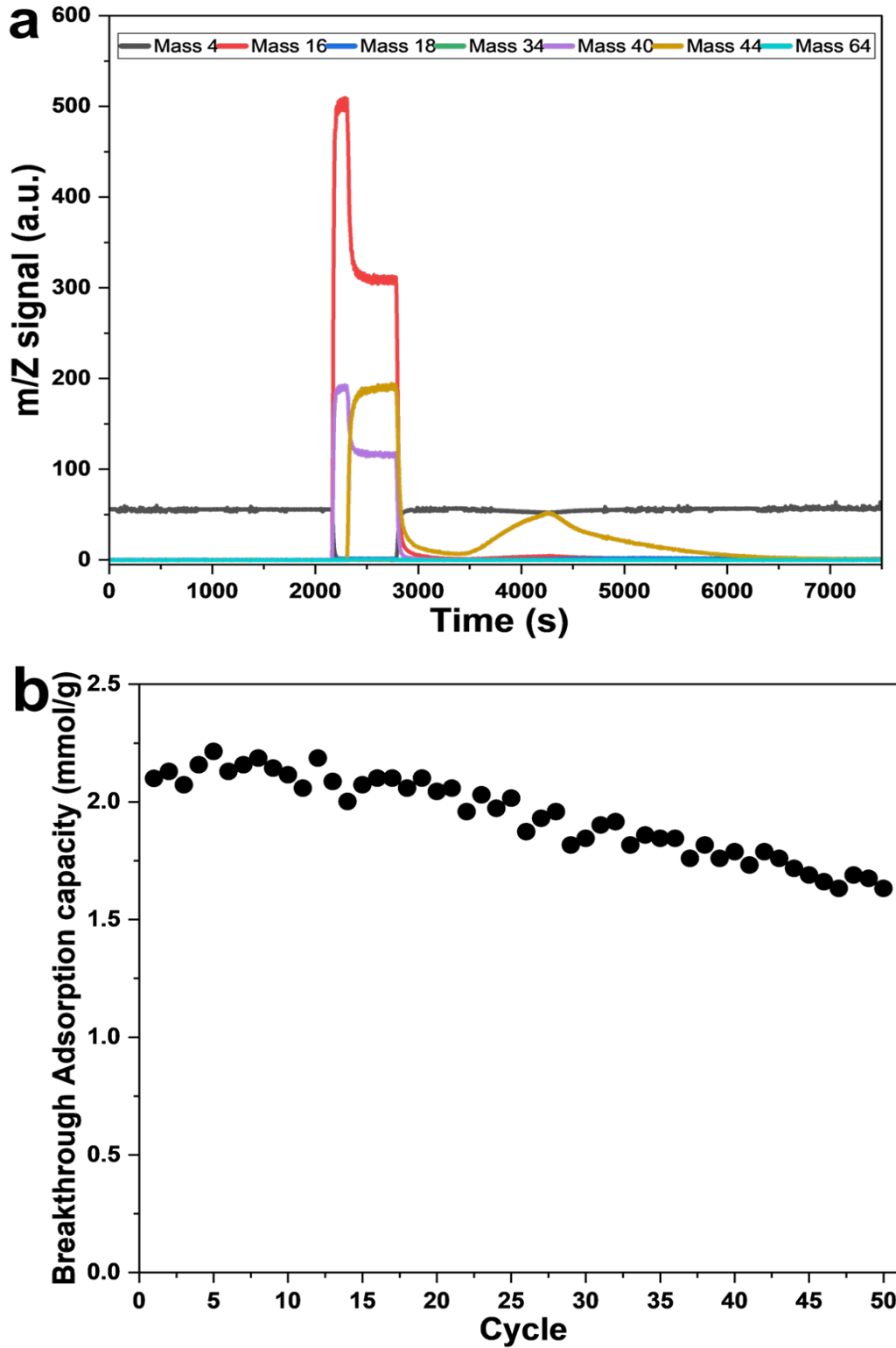


Figure 16: (a) Mass to charge ratio chart of different gas component during LFG upgrading cycle (b) CO₂ breakthrough capacity of PEI-HP2MGL during adsorption-desorption cycles in raw landfill gas.

Images of the sample before and after the 50 adsorption-desorption cycles (Figure 17), showed a pronounced color change in the adsorbent. This color change is related to continuous heat treatment due to the sample regeneration. Additionally, the spent adsorbent is shown to maintain the structural properties and potential changes may be due to chemical interaction with impurities or long-term exposure to CO₂ during the adsorption-desorption cycles.

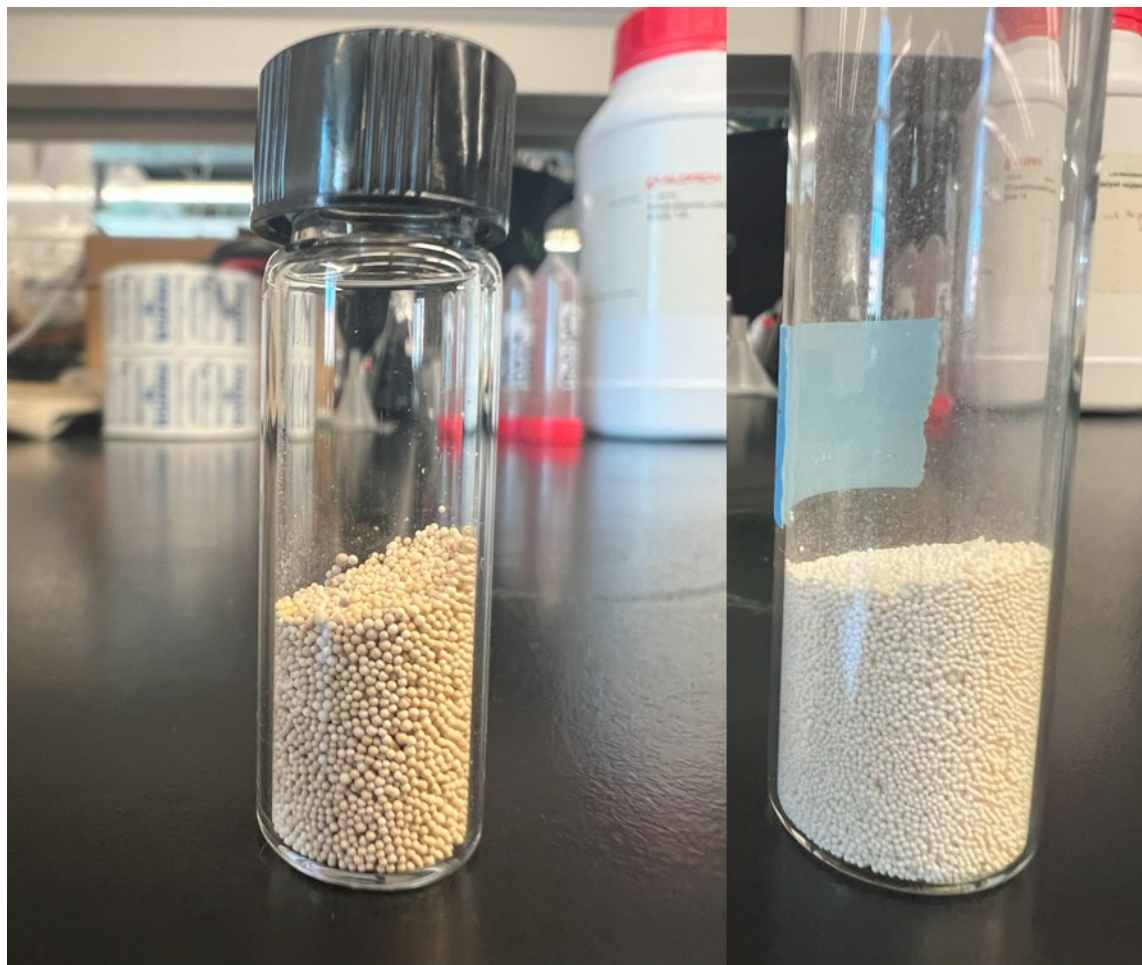


Figure 17: Picture of PEI-HPMGL before (Right) and after 50 adsorption-desorption cycles (Left).

Fourier Transform Infrared (FTIR) spectroscopy provided crucial insights into the structural changes and chemical interactions occurring within the PEI-modified resin adsorbents during landfill gas upgrading operations. The FTIR spectrum of fresh PEI-modified resin shown in Figure 18, revealed characteristic vibrational bands indicative of both amine functionalization and the polymeric backbone structure. The primary amine functionality was evidenced by

distinctive N-H stretching vibrations appearing at 3360-3310 cm^{-1} (asymmetric) and 3280-3250 cm^{-1} (symmetric), accompanied by N-H bending modes at 1650-1590 cm^{-1} and C-N stretching frequencies at 1090-1020 cm^{-1} . The polymer backbone structure was confirmed by C-H stretching vibrations at 2930-2850 cm^{-1} , C-C framework vibrations at 1480-1440 cm^{-1} , and C-O stretching bands at 1150-1070 cm^{-1} . Following 50 cycles of landfill gas exposure, a notable reduction in the intensity of amine-related bands was observed, particularly in the N-H stretching and bending regions, while the polymer backbone peaks remained relatively unchanged. This selective decrease in amine-related peak intensities suggests thermal cycling-induced amine leaching as the primary degradation mechanism, rather than structural deterioration of the polymer support. The preservation of the backbone spectral features indicates that the material maintains its structural integrity despite the gradual loss of active amine sites, which correlates with the observed 17% reduction in CO_2 breakthrough capacity over the cycling period. These results suggest using more amine adsorbents to achieve longer cycle times to minimize thermal degradation upon recycling.

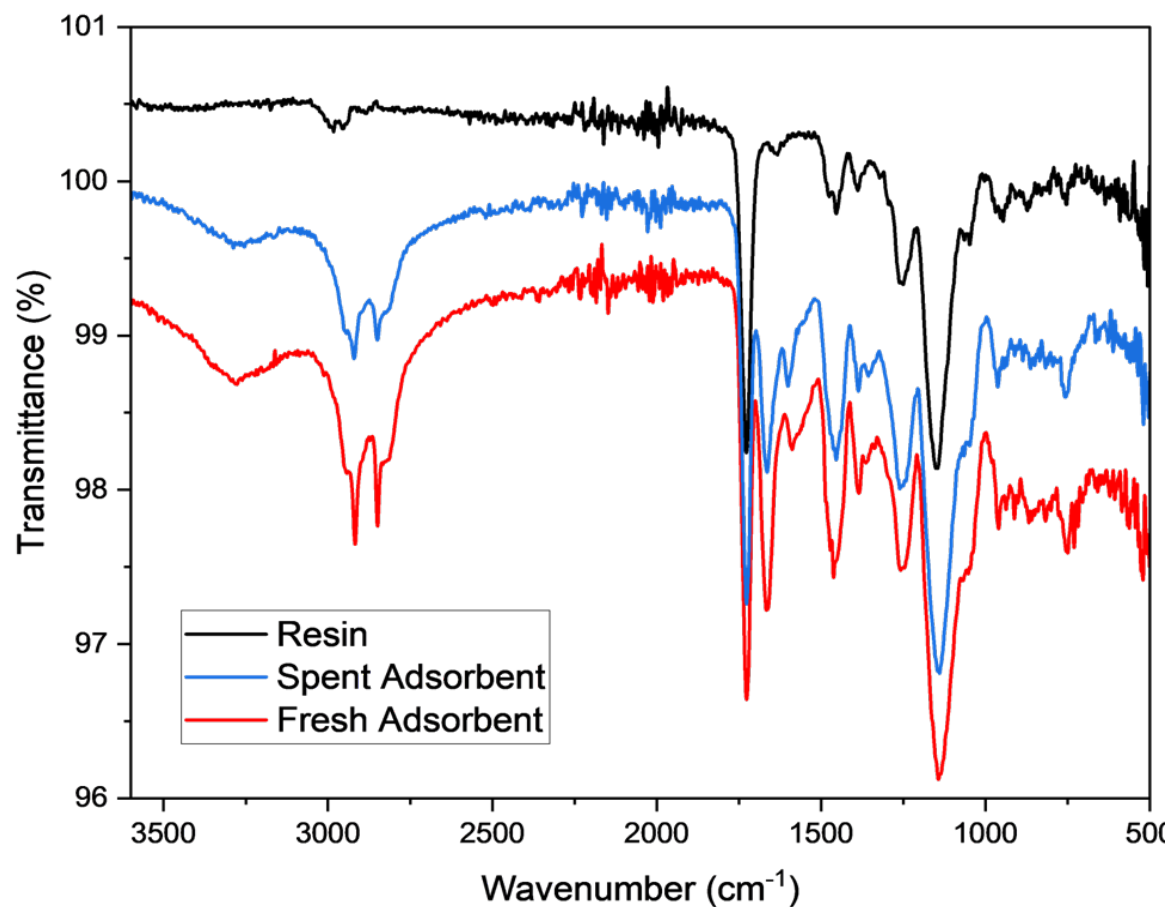


Figure 18: FTIR analysis of PEI-HP2MGL before and after 50 adsorption-desorption cycles.

Scanning electron microscopy (SEM) analysis was conducted to examine the morphological characteristics of the PEI-modified resin adsorbents before and after exposure to 50 cycles of landfill gas upgrading operations. As in Figure 19, the pristine material exhibited well-defined spherical particles with uniform size distribution and smooth surface texture, with occasional surface features attributed to the PEI modification process. Following 50 adsorption-desorption cycles under real landfill gas conditions and thermal cycling between 30°C and 100°C, the adsorbent demonstrated remarkable morphological stability, maintaining its spherical geometry with no evidence of particle fragmentation, deformation, or significant surface erosion confirmed by Figure 20. High-magnification examination revealed minimal changes in surface texture, though slight variations in surface roughness were observed, likely due to repeated thermal cycling and gas-solid interactions.

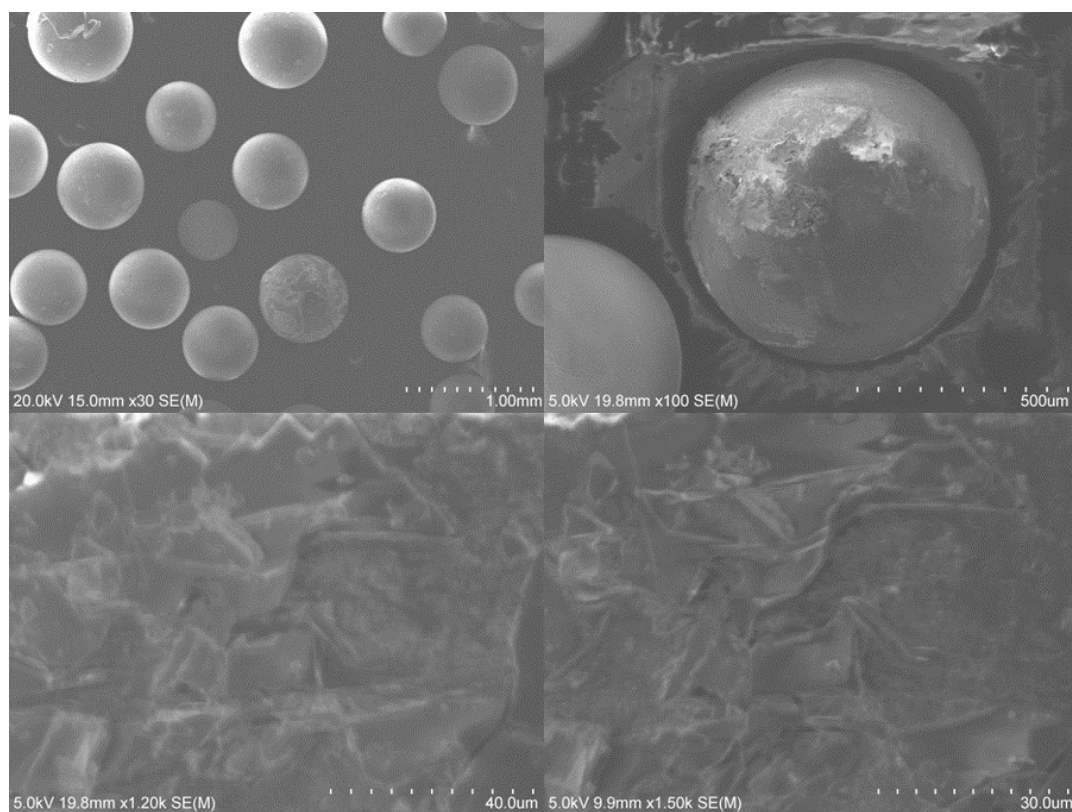


Figure 19: Scanning electron microscope (SEM) images of synthesized adsorbents.

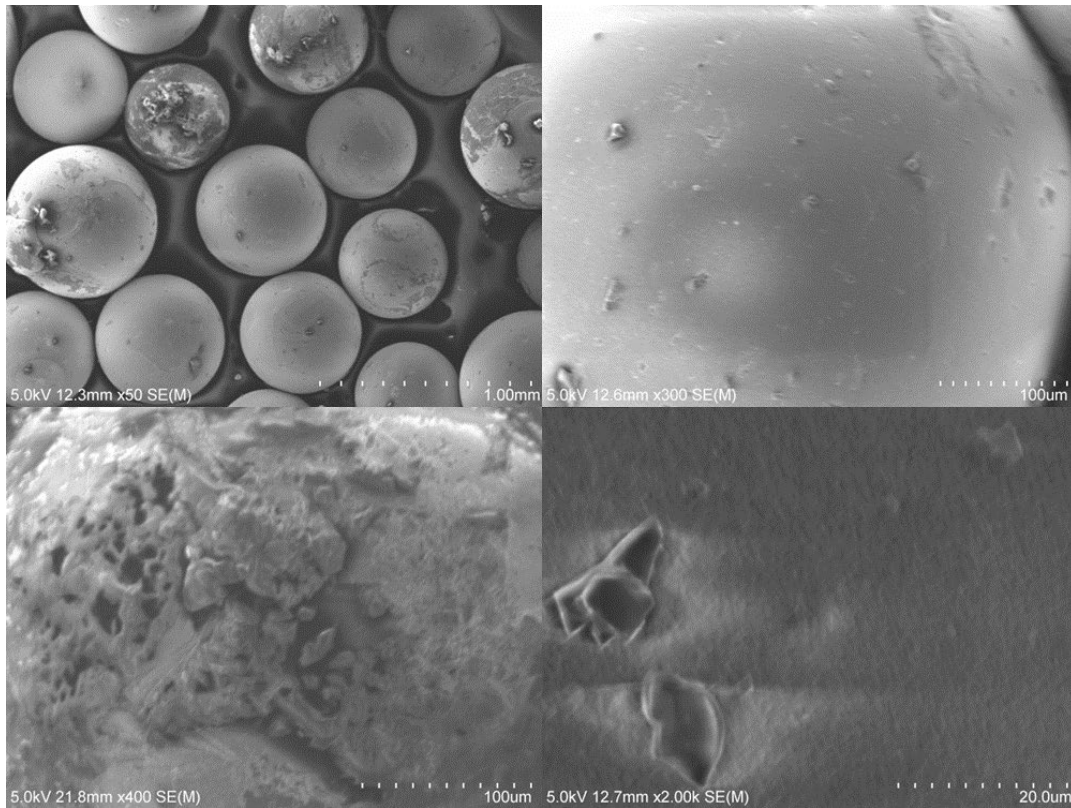


Figure 20: Scanning electron microscope (SEM) images of synthesized adsorbents after 50 adsorption-desorption cycles.

4.2. Techno-Economic Analyses

The pressure drop analysis across the adsorbent bed revealed significant implications for system design and operational costs. Theoretical calculation using the Ergun equation demonstrated a substantial pressure drop of 3.13 bar across the fixed bed, necessitating the use of high-capacity compressors rather than simple blowers for biogas circulation. This pressure drop, primarily attributed to the current particle size distribution and bed packing characteristics, represents a crucial parameter affecting both capital and operating costs. The techno-economic analysis is presented in Table 7 revealed a total biomethane production cost of \$123.75 per thousand cubic meters, positioning this technology competitively within the current market landscape. A detailed breakdown of operational costs identified regeneration energy as the dominant contributor, accounting for more than one-third of the total production expenses. The thermal swing process, despite utilizing a relatively modest temperature difference of 70°C between adsorption (30°C) and regeneration (100°C), requires significant steam consumption for

heating and nitrogen for cooling. The analysis demonstrated that the combination of adsorbent replacement costs and regeneration energy represents the largest cost component in LFG upgrading via the temperature swing adsorption process.

When compared to previous cost estimates, the current analysis shows approximately a 30% increase in total production costs. This increase primarily stems from two factors: the incorporation of additional compression requirements based on more accurate pressure drop predictions, and the integration of nitrogen cooling systems for enhanced process control. Despite this cost increase, technology maintains competitive advantages over conventional upgrading methods when considering the total value proposition, including higher methane recovery rates and reduced environmental impact. The economic model suggests that optimization of particle size could significantly reduce compression costs, potentially decreasing total production costs by 15-20%. Additionally, the analysis identified opportunities for cost reduction through improved heat integration and optimization of the regeneration cycle timing.

The potential revenue from a landfill gas upgrading unit can be realized through two primary avenues: (1) selling renewable natural gas (RNG) and (2) leveraging carbon footprint reduction value. As of October 2024, the price of natural gas, based on Henry Hub data, stands at \$79.86 per 1,000 m³ (\$110 per ton)[56]. Additionally, carbon credit represents a significant revenue source. Carbon credits can be accessed through governmental incentives, such as the 45Q Carbon Tax Credit, and participation in carbon credit market trading. The 45Q Carbon Tax Credit, designed for projects capturing carbon emissions, offers values ranging from \$12 to \$180 per metric ton of CO₂e[57]. Another federal incentive, the 45Z Clean Fuel Production Tax Credit, supports the production and sale of low-emission transportation fuels[58]. It provides a base rate of \$0.20 per gallon equivalent for non-aviation fuel, increasing to \$1.20 per gallon equivalent if prevailing wage and apprenticeship requirements are met. Carbon credit market trading has also become increasingly popular. Companies are allocated specific emissions quotas, with the ability to sell unused allowances to others. Current carbon credit prices vary widely, from as low as \$6 per ton (set by some financial service companies) to as high as \$40 per ton, as proposed by energy companies, economists, and climate experts[59, 60].

Table 7: Economic Breakdown of TSA Landfill Gas upgrading Unit.

Per 1000 m ³ of Biomethane	
	Updated
Operating cost of Steam	\$ 36.55
Annualized Vessel Cost	\$ 2.92
Operating cost of compressor	\$ 0.20
Annualized Compressor Cost	\$ 18.83
Adsorbent capital cost	\$ 33.08
Operating labor cost	\$ 21.09
Waste disposal cost	\$ 0.17
Operating cost of cooling N ₂	\$ 10.91
Overall cost	\$ 123.75

4.3. Life Cycle Assessment

4.3.1. Impact Assessment and Interpretation

Table 8 shows the life cycle GHG emissions measured in kilograms of CO₂ equivalent per kilogram of biogas. This approach allows the comparison between different pathways and technologies of LFG upgrading, in this case, comparing the use of PEI adsorbents for biogas upgrading with Pressure Swing Adsorption technology (considering activated carbon as adsorbents). The acronyms SC1, SC2, SC3 and SC4 are used to represent scenarios 1, 2, 3 and 4, respectively. SC1 and SC2 represent scenarios created using PEI adsorbents to produce compressed natural gas and liquefied natural gas.

Table 8: GHG emissions in kg CO₂e/kg biogas for CNG and LNG. Flaring is considered the counterfactual scenario.

Scenario	Life Cycle GHG Emissions [kgCO ₂ e/kg biogas]
SC1 (LFG-to-CNG using PEI)	0.1816
SC2 (LFG-to-LNG using PEI)	0.2750
SC3 (LFG-to-CNG using PSA)	0.7901
SC4 (LFG-to-Flare) Counterfactual	1.5022

Based on the results presented in Table 8, it can be noted that SC1, using PEI adsorbents to produce compressed natural gas shows the lowest GHG emissions in comparison to the other scenarios. SC1 accounts for a life cycle GHG emissions reduction of -0.6085 kg CO_{2e}/kg biogas in comparison with when pressure swing adsorption is used. This was expected, since PSA technologies show a higher percentage of methane leakage (3.5%) in comparison with amine adsorbents (0.07%), as mentioned in Major inventory data. When the counterfactual scenario is considered (LFG-to-Flare), a life cycle GHG emissions reduction of -1.3206 kg CO_{2e}/kg biogas is achieved considering the comparison with SC1. In comparison with the pathway to produce compressed natural gas reported in literature [54], scenario 1 also remains a viable route to reduce GHG emissions (-0.968 kg CO_{2e}/kg biogas) when taking into account the environmental impacts of the pathway proposed.

Among the LFG management scenarios presented, flaring has the highest life cycle GHG emissions with 1.5022 kgCO_{2e}/kg of biogas. Higher emissions for the counterfactual scenario are due to the flaring efficiency of 91.1% considered in this work.

When the functional unit of 1MJ of energy produced is used, the results presented in Table 9 are obtained. The Life Cycle GHG emissions associated with flaring of LFG (counterfactual scenario) are equal to 61.76 gCO_{2e}/MJ. In the table below, this value is considered to determine the credits from avoiding flaring LFG. The avoided emissions from flaring are the same for all the scenarios, and the difference shown in SC2 happens due to the difference in the amount of energy produced, since for LNG, some losses (boil-off) should be taken into account [50].

Table 9: GHG emissions in gCO_{2e}/MJ. Credits for avoiding flaring are considered.

	Life Cycle GHG Emissions (gCO _{2e} /MJ)	Credits from avoiding flaring (gCO _{2e} /MJ)	Net emissions (gCO _{2e} /MJ)
SC1 (LFG-to-CNG using PEI)	6.31	-61.76	-55.44
SC2 (LFG-to-LNG using PEI)	9.56	-58.05	-48.490
SC3 (LFG-to-CNG using PSA)	27.47	-61.76	-34.29

LFG-to-CNG [54]*	21.7	-61.76	-40.06
CNG NA NG [61]**	26.0	-	26.0

* The credits for avoiding flaring emissions in Poddar et al. (2023)'s work reflects re-calculated results considering flaring efficiency of 91.1%, for comparison purposes.

** CNG North American fossil-derived natural gas (NA NG).

Based on the data presented in the previous table, when comparing CNG NA NG and SC1 there is a reduction in net emissions of - 81.44 gCO_{2e}/MJ. This difference shows the effects on life cycle GHG emissions of using fossil natural gas over the process proposed using PEI adsorbents.

In addition, scenarios 1 and 2, which used amine adsorbents are the ones that show the lower life cycle GHG emissions in comparison with other scenarios. The difference between the net emissions for SC3 and SC1 (Pressure swing adsorption versus PEI adsorbents) is equal to - 21.1568 gCO_{2e}/MJ.

These results show that SC1 is a promising pathway to produce CNG using landfill gas, although, as reported previously by Poddar et al. [54], the economics also needs to be analyzed when comparing waste-to-energy technologies including avoided emissions.

4.3.2. Sensitivity Analysis

Since methane leakage in landfill gas upgrading technologies is a major factor that affects GHG emissions due to the global warming potential associated with methane emissions, this variable was analyzed for sensitivity analysis of two pathways studied previously (SC1 and SC3), as can be seen in Figure 21

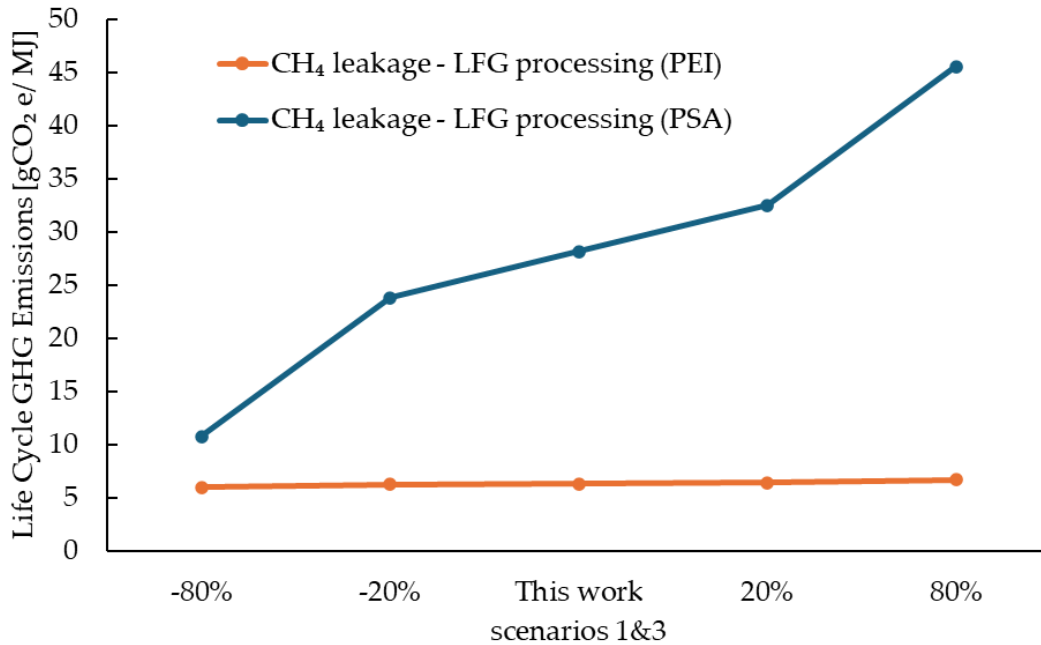


Figure 21: Sensitivity analysis to assess the effect of changing values (+20 %, + 80%, -20%, and + 80%) in the methane leakage percentage according to different pathways.

The results presented in Figure 21 show that since Pressure Swing Adsorption technologies have a higher methane leakage percentage (3.5%) in comparison with amine process (0.07%) that usually operates at lower pressures, the effects of changing values ($\pm 20\%$ or $\pm 80\%$) for the leakage percentage, reports a visually more prominent change (increase or decrease) in Life Cycle GHG Emissions for PSA. The scenario that uses PEI as adsorbents show a slight change in the GHG emissions with an increase of 0.3482 gCO₂e/MJ when comparing the base case (this work scenario 1) and + 80% change. This analysis emphasizes the importance of monitoring and improving landfill gas technologies to minimize the environmental impacts that methane leakage can cause.

4.3.3. Impact of the carbon intensity of the electricity grid

Figure 22 represents the impacts of varying the electricity grid mix. For this purpose, different grid mixes were analyzed: NPCC (Northeast Power Coordinating Council), FRCC (Florida Reliability Coordinating Council), ASCC (Alaska Systems Coordinating Council), U.S. Mix, and Solar (Electricity derived from grid-connected PV + battery system). It can be observed that when the carbon intensity of the grid is low the reduction in GHG emissions for SC1 and SC2 are higher than when the electricity grid shows a higher carbon intensity.

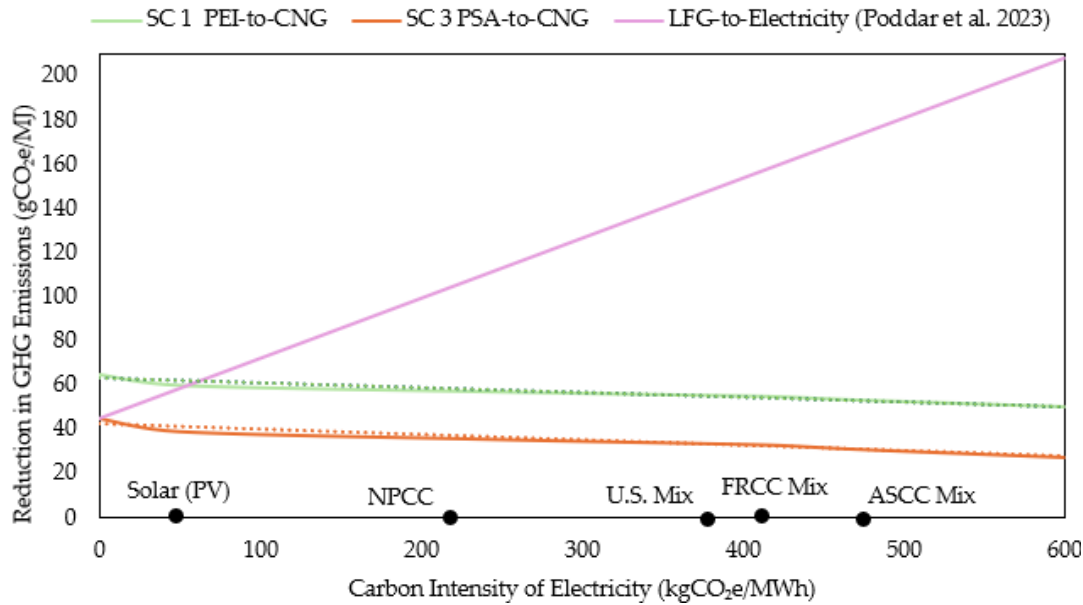


Figure 22: Carbon Intensity of Electricity using different grid mixes.

In addition, it is also possible to infer that SC1 independently from the grid mix used, is a pathway that contributes to higher reductions in GHG emissions in comparison to SC3, using Pressure Swing Adsorption. As reported by Poddar et al.[54], as the grid decarbonizes, the LFG-to-Electricity pathway will remain a viable Waste-to-Energy option in terms of reduction of GHG emissions, as can be seen in Figure 22. It is important to emphasize that the results presented above consider only environmental aspects, and economic conclusions may favor some pathways over others.

5. CONCLUSIONS AND FUTURE WORK

The experimental work showed that PEI-modified resin adsorbents were resynthesized and demonstrated reproducible CO₂ uptake capacity. In addition, LFG upgrading was performed for 50 adsorption-desorption cycles in the presence of impurities, showing promising results.

Regarding the techno-economic analysis, the pressure drop of ~3 bar indicates the need to pelletize adsorbent material before implementation. Furthermore, adsorbent purchase and regeneration costs represent the largest cost incurred for LFG upgrading via the TSA process.

Environmental analysis through the Life Cycle Assessment showed that the use of PEI adsorbents reduces significantly the life cycle GHG emissions in comparison with PSA and flaring. The difference between the scenario using PSA and PEI adsorbents is equal to 21.15 gCO_{2e}/MJ, and PEI adsorbents stand out by their lower GHG emissions. In addition, LFG-to-CNG using PEI is a promising pathway to reduce the reliance on fossil fuels, being responsible for 19.68 gCO_{2e}/MJ less GHG emissions than the North American compressed fossil Natural Gas.

The suggested future work includes the investigation of the amine capacity reduction mechanism in extended real LFG usage, the analysis of the impact of adsorbent pelletization and particle size on CO₂ adsorption capacity, and selectivity in LFG upgrading. The study of the effect of water partial pressure in feed LFG on CO₂ separation potential and long-term stability are also important points to be taken into consideration. While using large pellets would impact the kinetic uptake, it would lower the pressure drop and the large cost of the compressor. This would also enable longer cycle times by lessening the impact of pressure drop, which should negate deactivation via the thermal regeneration step. Optimization of these factors is a priority in the future.

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