Review

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Design Implications of Headspace Ratio V_{HS}/V_{tot} on Pressure Stability, Gas Composition and Methane Productivity in Batch Anaerobic Digesters

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Design Implications of Headspace Ratio V_{HS}/V_{tot} on Pressure Stability, Gas Composition and Methane Productivity in Batch Anaerobic Digesters

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Abstract

Headspace (HS) in anaerobic batch biodigesters is a critical design parameter that modulates pressure stability, gas–liquid equilibrium, and methanogenic productivity. This systematic review, guided by PRISMA 2020, analyzed 84 studies published between 2015 and 2025, of which 64 were included in the qualitative and quantitative synthesis. The interplay between headspace volume fraction V_{HS}/V_{tot}, operating pressure, and normalized methane yield was assessed, explicitly integrating safety and instrumentation requirements. In laboratory settings, maintaining a headspace volume fraction (HSVF) of 0.30-0.50 with continuous pressure monitoring P(t) and gas chromatography reduces volumetric uncertainty to below 5-8% and establishes reference yields of 300-430 NmL CH4 gVS^{-1} at 35 °C. At pilot scale, operation at 3-4 bar absolute increases the CH_4 fraction by 10-20 percentage points relative to ~1 bar, while maintaining yields of 0.28-0.35 L CH_4 $gCOD^{-1}$ and production rates of 0.8-1.5 Nm^3 CH_4 m^{-3} d^{-1} under OLRs of 4-30 kg COD m^{-3} d^{-1}, provided pH stabilizes at 7.2-7.6 and the free NH_3 fraction remains below inhibitory thresholds. At full scale, gas domes sized to buffer pressure peaks and equipped with continuous pressure and flow monitoring feed predictive models (AUC > 0.85) that reduce the incidence of foaming and unplanned shutdowns, while integration of desulfurization and condensate management keep corrosion at acceptable levels. Rational sizing of HS is essential to standardize BMP tests, correctly interpret the physicochemical effects of HS on CO_2 solubility, and distinguish them from intrinsic methanogenesis. We recommend explicitly reporting standardized metrics (Nm^3 CH_4 m^{-3} d^{-1}, NmL CH_4 gVS^{-1}, L CH_4 $gCOD^{-1}$), absolute or relative pressure, HSVF, and the analytical method as a basis for comparability and coupled thermodynamic modeling.

Keywords: anaerobic digestion; headspace; methanogenesis; volumetric ratio; batch biodigesters

1. Introduction

Batch anaerobic digestion (AD) has become an essential tool in research on the valorization of agro-industrial organic waste, allowing for the evaluation of biodegradability and biochemical methane potential (BMP) of different substrates under controlled conditions (Y. Liu et al., 2024). In these systems, the biodigester is loaded only once with substrate and inoculum and hermetically sealed during the fermentation period, enabling the production and accumulation of biogas without continuous feeding or discharge (Mekwichai et al., 2024). Although this operating scheme simplifies control and promotes experimental reproducibility, it introduces a frequently underestimated design parameter: headspace (HS), defined as the gas volume available above the liquid phase of the reactor (Hmaissia et al., 2025).

The HS (hybrid storage) plays critical roles that go beyond mere gas accumulation. From a physicochemical perspective, it regulates internal pressure, gas solubility, and the equilibrium between the liquid and gas phases (CO_2, CH_4, H_2S, NH_3), all of which are governed by Henry's law and operating conditions (Liao et al., 2025). A large gas volume buffers pressure variations and facilitates sampling, but it can induce excessive CO_2 outgassing, raise the pH, and alter the carbonate-bicarbonate equilibrium, increasing the risk of inhibition by free ammonia in nitrogen-rich substrates. Conversely, a reduced HS increases the partial pressure of gases, promotes their dissolution in the liquid phase, and can alter mass transfer kinetics and biogas composition (Mihi et al., 2024). This complex balance makes the HS a direct determinant of the efficiency, stability, and safety of the anaerobic process (Wani & Parveez, 2025).

The design of the HS varies substantially depending on the scale and purpose of the reactor (Raposo et al., 2020). In laboratory BMP tests, volume fractions of 30-50% are typically used to ensure stable pressure and facilitate correction of measurements to standard conditions (Filer et al., 2019). In contrast, in pilot or industrial digesters, the HS is maintained between 10-25%, incorporating flexible domes or external gasometers that dampen pressure spikes and reduce structural risks (Stan et al., 2018). However, there is no consensus on the optimal sizing, as the physicochemical conditions, substrate composition, and agitation regimes nonlinearly alter the gas-liquid interaction and the volumetric methane yield (Naji et al., 2024).

Recent literature shows a growing interest in quantitatively modeling the effects of HS. Extensions of the ADM1 model (Anaerobic Digestion Model No.1) have explicitly incorporated the gas phase, demonstrating that variations in HS pressure modify pH dynamics, CO_2 solubility, and the availability of volatile intermediates (Catenacci et al., 2024). This approach has allowed correlation of the fraction V_{HS}/V_{tot} with methane yield and reactor stability parameters, opening the possibility of optimizing the design through coupled thermodynamic simulation (Karsten et al., 2025). However, the lack of a comparative systematization of scales, operating strategies, and quantitative results limits the ability to extrapolate conclusions and standardize experimental protocols (Li et al., 2025).

Therefore, this review proposes a comprehensive and comparative synthesis of HS behavior in batch biodigesters. Verifiable evidence on the effects of headspace volume fraction, pressure, and methane production on operational safety is compiled and analyzed to identify quantitative patterns and design criteria that support modeling and scale-up of anaerobic digestion systems. In this way, the work seeks to bridge the gap between empirical practice and theoretical-predictive foundations, providing a robust scientific basis for the rational design of more efficient and sustainable biodigesters.

2. Systematic Review Methodology

This review was developed following the guidelines of the PRISMA 2020 protocol (Preferred Reporting Items for Systematic Reviews and Meta- Analyses) (Yepes-Nuñez et al., 2021), with the purpose of ensuring transparency, reproducibility and traceability in the collection, selection and analysis of scientific literature related to the design, operation and modeling of headspace in batch biodigesters.

2.1. Search Strategy and Databases

The literature search was conducted between July and September 2025 in Scopus and PubMed. Search equations were designed a priori, combining controlled descriptors and free terms with Boolean operators, aimed at capturing studies on anaerobic digestion and the influence of headspace on biogas generation and measurement. The search equations combined keywords and Boolean operators under the general format:

For Scopus

(“anaerobic digestion” OR “biochemical methane potential” OR “BMP test”) AND (“headspace” OR “gas phase” OR “gas volume ratio” OR “V_{HS} /V_{tot} ”) AND (“biogas yield” OR “methane production” OR “pressure” OR “CO_2 solubility” OR “gas-liquid equilibrium”).

For PubMed

("anaerobic digestion"[Title/Abstract] OR "biochemical methane potential"[Title/Abstract] OR "BMP test"[Title/Abstract])

AND ("headspace"[Title/Abstract] OR "gas phase"[Title/Abstract] OR "gas volume ratio"[Title/Abstract] OR "Vhs/Vtot"[Title/Abstract])
AND ("biogas yield"[Title/Abstract] OR "methane production"[Title/Abstract] OR "pressure"[Title/Abstract] OR "CO^2 solubility"[Title/Abstract] OR "gas-liquid equilibrium"[Title/Abstract])

To maximize coverage, we included synonyms for headspace (e.g., "gas cap," "gas volume," "gas retention zone") and terms related to reactor scale (lab scale, pilot scale, industrial scale). No geographical or language restrictions were applied, although peer-reviewed articles in English and Spanish were prioritized.

2.2. Inclusion and Exclusion Criteria

Inclusion criteria:

- Peer-reviewed scientific articles published between 2015 and 2025.
- Experimental, comparative or modeling studies that explicitly report the headspace fraction (V_{HS}/V_{tot}) or related parameters (pressure, gas volume, CH_4 yield).
- Publications that present verifiable data on pressure, temperature, volume or composition of biogas.
- Book reviews or chapters with active DOI and verifiable access.

Exclusion criteria:

- Documents without quantitative information related to headspace: absence of (V_{HS}/V_{tot}), volume/gas phase ratio, measured pressure, or its impact on biogas/methane yield.
- Theses, technical reports or grey literature without peer review or verifiable DOI/URL, or without access to the full text.
- Duplicate records or studies with verifiable inconsistencies between text, tables and/or figures (e.g., discrepancies in (V_{HS}/V_{tot}), pressure or units).
- Studies evaluating aerobic digestion, composting, nitrification/denitrification, photofermentative processes, oxy-fermentations, or other non-anaerobic technologies; or anaerobic studies that do not address the measurement or effect of headspace on pressure, gas–liquid equilibrium, or CH_4 yield.

2.3. Study Selection Process

The search strategy identified 416 records: Scopus (n = 388), PubMed (n = 24), and a manual search in Google Scholar (n = 4). After initial cleaning (duplicate removal and first screening by title), 272 references were submitted for evaluation. At this stage, 131 were excluded for thematic irrelevance, and 13 additional duplicates were removed, leaving 115 for screening by abstract (Figure 1).

In the abstract review, 157 records were excluded for not meeting the required methodological and reporting criteria, leaving 64 articles to proceed to full-text evaluation. In this eligibility phase, 51 studies were excluded for the following reasons: they were not experimental or did not explicitly report the headspace fraction (V_{HS}/V_{tot}) or related parameters (pressure, gas volume, CH_4 yield) (n = 21); they lacked verifiable data on pressure, temperature, volume, or biogas composition (n = 23); or they were reviews/chapters without an active DOI or verifiable access (n = 7). Finally, 64 studies were included in the qualitative and quantitative synthesis.

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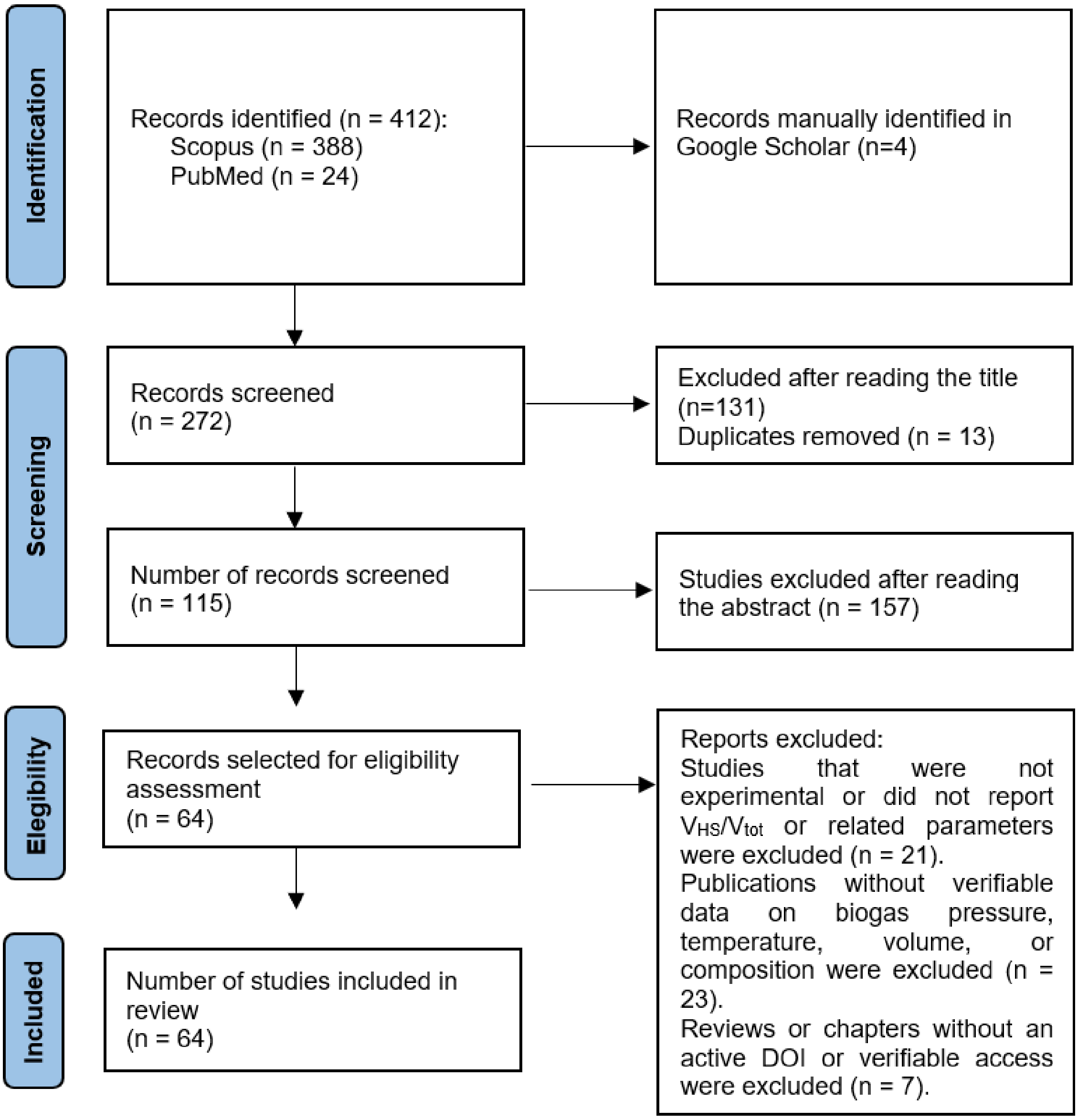

Figure 1. PRISMA 2020 flowchart of the selection process.

The diagram details the identification, screening, eligibility, and inclusion phases, with the counts at each stage and the reasons for exclusion in full text, in accordance with PRISMA 2020. The flow documents the transition from 416 initial records to 64 included studies.

2.4. Data Extraction and Validation

The following quantitative and operational parameters were extracted from each selected publication:

- Scale and type of reactor (BMP, laboratory, pilot, industrial).
- Primary substrate type.
- Volumetric fraction of headspace (V_{HS}/V_{tot}).
- Operating pressure and temperature.
- Biogas monitoring method (GC, NDIR, flow meters).
- Specific methane production (mL $CH_4 \cdot g^{-1}$ VS or L $CH_4 \cdot L^{-1} \cdot d^{-1}$).
- Reactor material and type of agitation.

The data were verified by cross-referencing the numerical information with the original sources and their DOIs. In the case of ranges or values reported under non- standard conditions, they were normalized to 101.3 kPa and 0 °C to ensure comparability of the results.

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2.5. Analysis and Synthesis of Information

A mixed-methods approach was used, combining narrative synthesis and quantitative analysis. Studies were grouped by scale of operation and substrate type, among other relevant variables. The verified data were structured in comparative matrices, and the effects of headspace fraction V_{HS}/V_{tot} and operating pressure on methanogenic yield were analyzed to interpret the influence of headspace on CO_2 solubility. Finally, the review was supplemented with safety considerations, given their impact on the design and operation of biodigesters.

2.6. Limitations of the Review

Despite the rigorous application of the PRISMA protocol, it is acknowledged that the available literature exhibits heterogeneity in the way headspace volume, internal pressures, and gas correction conditions are reported. Some studies lack unit standardization or sufficient information to calculate the ratio V_{HS}/V_{tot}.

However, the convergence of multiple experimental sources and reviews made it possible to identify consistent trends that support the proposed ranges and the predictive equation presented in section 7.

3. Technical Fundamentals of Headspace

In batch-operated biodigesters, the HS constitutes the gaseous phase confined above the liquid digestion phase and plays a crucial role in the thermodynamics, gas-liquid mass transfer, acid-base equilibria, and operational safety of the system. From a macroscopic perspective, the internal pressure results from the accumulation of gas moles according to the equation of state, while at the species level, partial pressures regulate solubility equilibria and the direction of transfer flows. These interactions are modulated by temperature, reactor geometry, the volumetric ratio of HS to the total volume, and venting and storage strategies. Table 1 synthesizes the key physicochemical parameters, design relations, and safety considerations, with primary references; their relevance to design and operation is discussed below.

Batch biodigesters with moderate pressures and under mesophilic or thermophilic conditions, the gas behavior can approximate that of an ideal gas, such that the pressure P in the HS satisfies $PV_{HS} = n_gRT$, where n_g is the total moles accumulated, V_{HS} is the HS volume, and T is the temperature (Awasthi et al., 2023). This relationship reveals the buffering role of a sufficiently large V_{HS}: for the same biogas production pulse, the pressure increase is smaller than the larger V_{HS} is, which reduces the risk of overpressure and improves the repeatability of measurements. This effect can be expressed as a gaseous "capacitance" $Ce = (\partial ng/\partial P)T = V_{HS}/(RT)$, which increases linearly with VHS and T; in systems with domes or flexible gasometers, the elasticity of the container increases the effective capacitance, attenuating pressure spikes (Siciliano et al., 2021). However, the reduction of partial pressure by frequent venting or operation at low backpressure favors the shift of the gas-liquid equilibrium towards the gas phase, intensifying the stripping of volatile acid species.

Dalton's law allows the total biogas pressure to be partitioned into partial pressures, Pi = yi P. Combined with Henry's law, this enables quantification of the solubility of gases such as CO_2 and H_2S, expressed as $C_i^* = P_i/H_i(T)$. The Henry constant Hi(T) decreases with temperature following a van't Hoff-type relationship, $d(\ln H)/d(1/T) \approx \Delta H_{sol}/R$; consequently, under thermophilic conditions, the lower solubility of CO_2 and H_2S increases their volatility, altering the biogas composition and the acid–base status of the liquid digestion phase. For ammonia, gas-liquid partitioning depends on the NH_4^+/ NH_3 equilibrium, whose pKa ≈ 9.25 at 25 °C and decreases with temperature. Therefore, increases in pH and T raise the fraction of free NH3, entailing a greater risk of biological inhibition (Gao et al., 2023). These interactions are modulated by the carbonate system, characterized by pKa1 ≈ 6.35 and pKa2 ≈ 10.33 (Meybodi et al., 2024). CO_2 stripping tends to raise pH and effective alkalinity, shifting the CO_2(aq)- H_2CO_3 - HCO_3^- - CO_3^{2-} equilibria. Although this phenomenon can contribute to deacidification during the initial phase of acidogenesis, it also

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increases the fraction of free NH_3 and, depending on pH, alters reduced-sulfur speciation (H_2S/HS^-), with implications for both biological toxicity and system corrosion (Tzenos et al., 2023).

From a design perspective, the volumetric ratio V_{HS}/V_{tot} represents a fundamental compromise between operational safety, gas metrology, and the structural compactness of the biodigester. In laboratory systems, such as BMP bottles and experimental reactors, typical ratios between 0.30 and 0.50 are recommended to facilitate sampling and prevent overpressures, always correcting biogas volumes to standard conditions and discounting water vapor according to guidelines such as VDI 4630 and equivalent methodological consensus (Strömberg et al., 2014). At pilot and farm scales, internal ratios of 0.10 to 0.25 are commonly used, complemented by domes or flexible storage systems that increase the effective gas capacitance $C_e = V_{HS}/(RT)$, providing mechanical damping and reducing pressure fluctuations (Scarlat et al., 2018). The reactor geometry, particularly the height-to-diameter ratio and the arrangement of baffles, along with the nature of the materials, influences the hydrodynamics, foam formation, and selective permeability to trace compounds. In this context, materials such as stainless steel, fiberglass reinforced plastic (FRP) and EPDM/PTFE elastomer membranes are selected for their chemical compatibility against acid gases such as H_2S and volatile bases such as NH_3, although permeability, thermal resistance and UV radiation aging must be considered, factors that directly affect the durability of the system (Situmorang et al., 2020).

In terms of safety, the sizing and certification of relief valves must ensure that the setpoint remains below the design pressure P_{design}, with controlled biogas flow to flares, consumers, or venting systems, and the incorporation of backflow prevention devices to avoid flame flashbacks, in accordance with NFPA (2021) and ATEX Directive 2014/34/EU (2014). Similarly, environmental monitoring of H_2S and CH_4, proper condensate management, and early desulfurization through biological oxidation, adsorption on ferric oxides, or chemical scrubbing are effective strategies for mitigating occupational risks and reducing corrosion (Bhowmik & Sabharwall, 2023). Ultimately, continuous instrumentation of pressure, temperature, and composition in the biogas storage system is not only a regulatory safety requirement but also essential for accurately interpreting the stability, performance, and efficiency of the biogas process.

Table 1. Physicochemical and design parameters relevant to headspace in batch biodigesters and safety considerations.

Category	Parameter/relationship	Typical value/expression	Technical comment	References
Gas status	Equation of state	$PV_{HS} = n_g RT$	Ideal gas equation valid at moderate pressures; it is recommended to correct for water vapor when normalizing dry biogas	(Angelidaki et al., 2018)
Gaseous capacitance	$Ce = (\partial n_g/\partial P)T$	$Ce = V_{HS}/(RT)$	Capacitance increases with dome volume; it reduces pressure variation $\frac{dP}{dt}$. Flexible domes increase effective capacitance.	(Yang et al., 2024)
Partial pressure	Dalton's Law	$P_i = y_i P$	Determine the equilibrium concentration C_i^* using Henry's Law and the mass transfer driving force	(Su et al., 2020)
Henry's constant (CO_2)	$C^*_{CO2} = \frac{P_{CO2}}{H_{CO2}(T)}$	H_{CO2} (25 °C) ≈ 29 bar·m³·kmol⁻¹; d(ln H)/d(1/T) ≈ $\Delta H_{sol}/R$.	It decreases with temperature, increasing "stripping" in thermophilic.	(Sander, 2015)
Henry's constant (H_2S)	$C^*_{H2S} = \frac{P_{H2S}}{H_{H2S}(T)}$	H_{H2S} (25 °C) ≈ 1.0 bar·m³·kmol⁻¹	It exhibits high solubility. Speciation depends on pH (H_2S/HS^- equilibrium).	(Sander, 2015)

Balance	pKa,NH_4^+/NH_3	pKa ≈ 9.25 (25 °C), decrece con T	The fractionation of NH_3 free increases with pH and temperature; risk of biological inhibition at high values.	(Yirong et al., 2017)
Gas-liquid transfer	Gas-liquid mass transfer flow	$N_i = k_La(C - C^*)$	k_La ~ 10^{-3}-10^{-2} s^{-1} in sludge with solids; intermittent agitation improves k_La but may induce foaming.	(Prata et al., 2018)
Carbonate system	pK_{a1} /pK_{a2}	pK_{a1} ≈ 6.35; pK_{a2} ≈ 10.33 (25 °C)	"Stripping" raises pH and alkalinity; it interacts with the free ammonia balance.	(Sapunov et al., 2021)
Ranges V_{HS}/V_{tot}	Laboratory vs. pilot/farm	BMP: 0.30–0.50; Pilot/farm: 0.10–0.25	Compromise between metrological safety and structural compactness.	(Hafner et al., 2020)
Materials	Chemical compatibility	Stainless steel, GRP, EPDM/PTFE	Materials resistant to H_2S and NH_3; attention to permeability and thermal or UV aging of membranes.	(Pilarski et al., 2025)
Security	Relief and venting	Setpoint < P_{design}; non-return valve and torch.	Compliance with NFPA/ATEX regulations; CH_4 and H_2S monitoring; gas line condensate management.	(Luo et al., 2022)

Note. Symbols and abbreviations: P= total gas pressure (bar or Pa); V_{HS}=headspace volume (m^3); n_g= number of moles of gas (mol); R= universal gas constant (8.314 $J \cdot mol^{-1}.K^{-1}$); T= absolute temperature (K); C_e= gas capacitance, defined as $(\frac{\partial n_g}{\partial P})_T$($mol \cdot bar^{-1}$ or $mol.Pa^{-1}$); P_i= partial pressure of component i (bar or Pa); y_i= mole fraction of component $i$in gas phase (dimensionless); C_i^*= equilibrium concentration of component $i$in liquid phase ($mol.m^{-3}$); $H_i(T)$= temperature-dependent Henry's law constant ($bar.m^3.mol^{-1}$); ΔH_{sol}= molar enthalpy of solution ($J.mol^{-1}$); N_i= molar flow rate of component transfer i($mol \cdot m^{-2}.s^{-1}$); k_La= volumetric mass transfer coefficient (s^{-1}); C= concentration of the solute in the liquid phase ($mol.m^{-3}$); C^*= equilibrium concentration in the liquid phase ($mol.m^{-3}$); pK_a, pK_{a1}, pK_{a2}= negative logarithms of the dissociation constants of the acid-base system (dimensionless); V_{tot}= total volume of the reactor (m^3); P_{desing}= design pressure of the system (bar or Pa).

Material abbreviations:
PRFV = fiberglass reinforced plastic reinforced plastic);
EPDM = ethylene propylene diene monomer (a corrosion-resistant elastomer);
PTFE = polytetrafluoroethylene (commercially known as Teflon).

4. Influence of Headspace on Process Performance

The HS, defined by the free gas volume, internal pressure, and gas composition, is an operational parameter that modulates the physicochemical and microbiological equilibria in anaerobic digestion. The results summarized in Table 2 indicate that this variable affects methane production and rate, biogas composition, reactor stability, and the transfer of inhibitory or corrosive gases.

Table 2. Headspace in biogas batch systems and operational considerations.

Headspace conditions	Relevant results	Comment	Reference
BMP bottles: headspace 50, 90 and 180 mL (constant medium 70 mL)	Larger headspace volume means less pressure buildup; better biogas yield; relatively stable methane yield.	Methodological approach for BMP trials, showing free volume effect.	(Himanshu et al., 2017)

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Tests with coffee residues, cocoa husks and manure; headspace overpressures > 600 mbar	In coffee waste, overpressure >600 mbar reduced methane input; for other substrates there was no adverse effect in the 600-1000 -mbar range.	Evidence that headspace pressure impacts depending on the type of substrate.	(Valero et al., 2016)
Headspace pressure: 12.6 psi (~0.87 bar), 6.3 psi (~0.43 bar), 3.3 psi (~0.23 bar) and ambient	Pressure ~3 -6 psi improved COD production ~22 -36%, solubles ~9 -43%, volatile solids reduction ~14 -19% and methane +10 -31% vs control.	It shows that a moderate headspace pressure favors the hydrolytic/acidogenic phase and improves methanogenesis.	(Yan et al., 2017)
BMP trials: headspace fraction 0.25 (40 mL in 160 mL bottle) versus 0.75	Measurement error up to ~24% with headspace fraction 0.25; ~3% with fraction 0.75. Relative error in CH_4 increased with headspace pressure.	Evidence that free volume/headspace fraction has an impact on the accuracy of measurements.	(Hafner & Astals , 2019)
Headspace flushing test: N_2, N_2/CO_2 (80/20), without flushing	Flushing with 20% CO_2 increased methane production >20% in inoculum alone compared to pure N_2 flushing .	The effect of gas composition on headspace is more important than volume/pressure.	(Koch et al., 2015a)
Study of working volume-headspace ratio in BMP assays	They mention that headspace conditions affect biogas production; not much numerical quantification.	Recognition of the "Headspace Volume Fraction" (HSVF) as a design variable remains limited.	(Elsayed et al., 2022)
225 L reactor: headspace volume 40% versus 60%	At 40% headspace, VFA production is ten times greater than at 60%; changes in microbial community.	Although focused on VFA, it shows the impact of headspace volume on microbiology and performance.	(Di Leto et al., 2024)
BMP review: headspace in typical tests 10 mL to 1400 mL; headspace volume fraction % varies widely	It indicates that headspace varies between ~10 to ~76% of the total volume and that this variable should be considered in design.	It reinforces that the literature considers headspace as a variable, but with scattered data.	(Cabrita & Santos, 2023a)
Pilot reactor 265 L: headspace volume 50.0 L, 9.5 L, 1.5 L; micro-oxygenation for H_2S removal	H_2S removal of 99% with headspace 50 L or 9.5 L; fell to ≈15% when headspace reduced to 1.5 L.	It shows that the available volume of gas-headspace impacts H_2S transfer and removal.	(Ramos et al., 2012)
Test with relative pressure in the range 300-800 mbar (≈0.3-0.8 bar) in biogas/hydrogen	CH_4 > 3.9 mmol/L when relative pressure between 300 and 800 mbar; indirect pressure/headspace contributions.	Although focused on hydrogen, it provides data on the relative pressure of the gas-headspace in digestion.	(Mahmoodi-Eshkaftakia & Mockaitis, 2022)

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General review: digesting internal pressure, including headspace, is noted as a variable.	It indicates that the solubility of the gases (CO_2/CH_4) increases with pressure, which can increase CH_4 in free gas; but it also warns of negative effects of high pressure.	It supports the physical -and chemical basis of the pressure effect on headspace.	(Aworanti et al., 2023)
500 mL bottles: working volumes 125, 200, 300, 400 mL → corresponding headspace 80%, 60%, 40%, 20%	Reactors with lower working volume (greater headspace) produced a higher percentage of methane (~14-23 -% more than those with greater liquid volume)	It indicates that a larger volume of free gas (greater headspace) favors biogas/methane production in BMP.	(Vedat Yılmaz, 2017)
Chicken manure digestion batch ; air injection into the headspace (technique variation)	H_2S removal down to ~1015 ppm and CH_4 increase by 6.4% with air injection into the headspace.	Operational example of how headspace (gas) management improves biogas quality.	(Y. Song et al., 2020)
Food waste fermentation bed: headspace conditions T1 (self-generated), T2 (30% CO_2 + 70% N_2), T3 (90% CO_2 + 10% N_2)	T3 (90% CO_2 in headspace) gave a soluble yield of 0.81 g COD/g VS removal, significantly higher than others	Although it does not directly analyze methane, it shows that headspace composition (CO_2) affects acid and biogas yield.	(C. Liu et al., 2025)
Full-scale plant review mentions that headspace conditions influence the fermentation process, including headspace volume and pressure.	He points out that, although these effects are recognized, the literature does not quantify them well; he calls for research into the relationship between - headspace volume/pressure and biogas production.	It serves as an argument for the research gap on the topic.	(Kouzi et al., 2020)

Note: T1: self-generated (gas autogenerado por la fermentación, sin ajuste externo), T2: 30% CO_2 + 70% N_2 (headspace ajustado/flush con esa mezcla), T3: 90% CO_2 + 10% N_2 (headspace ajustado/flush con alta fracción de CO_2).

Regarding methane production and rate, studies agree that the volume and pressure of the HS alter both the measurement and the kinetics of the process. Himanshu et al. (2017)determined that by increasing the free volume of the HS from 50 to 180 mL in BMP tests, the internal pressure decreased and a higher apparent biogas production was obtained, without notable variations in the CH_4 fraction. This behavior is interpreted as an effect on gas compressibility and release, rather than on methanogenic activity. Hafner & Astals (2019). They corroborated this phenomenon by quantifying measurement errors of up to 24% when the HS represented only 25% of the total volume, showing that reduced gas fractions cause overpressure and delay in the volume reading.

The effect of pressure on bioconversion also depends on the substrate. Valero et al. (2016) They recorded decreases in methane in coffee residues when the overpressure exceeded 600 mbar, while no variations were observed in cocoa husks and manure, indicating a differential sensitivity related to organic composition and buffering capacity. Similarly, Yan et al. (2017). They showed that a moderate HS pressure (3-6 psi, 0.2-0.4 bar) increased the conversion of volatile solids and CH_4 between 10 and 31%, which suggests that slight gas confinement can intensify mass transfer between phases and improve the availability of soluble intermediates.

More recent results confirm this trend. Aragüés-Aldea et al. (2025) They used an initial pressure of 3.3 psi (~0.23 bar) in mixed reactors and observed an increase in methanogenic productivity, attributable to a more stable equilibrium between gas production and solubilization. Sharma et al. (2026)They analyzed digesters pressurized at 1.0 MPa, concluding that controlling the pressure of the

HS allows for intensified digestion by modifying the solubility of CO_2 and the temporary retention of CH_4, although high pressures can reduce the overall biogas volume. These findings are explained by Henry's solubility principle: as pressure increases, CO_2, being more soluble than CH_4, is preferentially transferred to the liquid phase, generating a residual biogas with a higher proportion of methane (Qian et al., 2025).

The composition of biogas is also influenced by the headspace gas. Koch et al. (2015) showed that an initial flush with N_2/CO_2 (80/20) increased methane production by more than 20% compared with pure N_2, indicating that the initial presence of CO_2 modulates the system's acid–base balance. Similarly, Liu et al. (2025) reported that a headspace with 90% CO_2 favored organic matter conversion (0.81 g COD per g VS removed) by redistributing carbon toward acidogenesis. These findings suggest that the initial headspace composition can steer metabolic pathways by influencing pH and the partial pressure of CO_2.

Reactor stability, assessed by pH and alkalinity, is indirectly linked to the magnitude of the headspace. A smaller gas fraction increases CO_2 dissolution in the liquid phase and carbonic acid formation, which can lower pH and reduce buffering capacity. Cabrita & Santos (2023) emphasized that experimental designs should report the working volume–to–headspace volume ratio, as its omission limits the interpretation of alkalinity and free NH_3 variations. Likewise, Aworanti et al. (2023) showed that high internal pressure alters NH_3 partitioning between phases, increasing its concentration in the liquid and, consequently, its inhibitory potential.

Foam and crust formation depend on the balance between gas release and bubble retention. Wu et al. (2023) observed that bottles with a larger headspace fraction (80%) produced 14–23% more methane than those with a smaller gas volume, a result associated with lower resistance to biogas release and a more continuous release rate. Although the available studies do not directly quantify foam, this behavior suggests that headspace plays a role in bubble rise dynamics and solids training.

Regarding gaseous and corrosive inhibitors, the relationship between headspace and H_2S removal has been experimentally demonstrated. Ramos et al. (2012) reported that H_2S removal efficiency dropped from 99% to 15% when headspace volume was reduced from 50 L to 1.5 L in micro-oxygenated reactors, evidencing mass-transfer limitations in confined spaces. Similarly, Song et al. (2020) introduced air into the headspace of reactors treating poultry manure and observed a decrease in H_2S (~1,015 ppm) along with a 6.4% increase in methane. These findings show that headspace control affects not only biogas production but also its quality and the corrosiveness of the surrounding environment.

Taking together, the evidence in **Table 2** shows that headspace volume and pressure govern the balance among gas solubility, mass transfer, and the digestate's chemical conditions. Intermediate gas fractions (0.50–0.75 of total volume) help minimize measurement errors and keep internal pressures within ranges that do not constrain biochemical processes (Hafner & Astals, 2019). In contrast, pressures above 1 bar or very small headspaces can cause excessive CO_2 dissolution, shift pH, and hinder biogas release. As noted by Kouzi et al. (2020), the lack of systematic reporting on these parameters limits predictive modeling of reactor performance. Therefore, future studies should quantitatively report headspace volume, operating pressure, gas composition, and stability indicators (pH, alkalinity, NH_3, VFA) to derive empirical patterns and thermodynamic models for optimizing this design variable.

5. Influence of Headspace According to the Scale of Operation

The contribution of HS to anaerobic digestion is strongly scale-dependent because gas capacitance, gas-liquid transfer, liquid-phase rheology, and control strategy all vary. In the laboratory, the ratio VHS/Vtot controls the system's compressibility and, by extension, the pressure response to gas production. Assuming ideal gas and a constant temperature of 35 °C, a 100 mL increase in CH_4 produced in a vial with VHS = 100 mL raises the absolute pressure by approximately 1 atm if there is no venting, while the same pulse in VHS = 300 mL increases the pressure by approximately 0.33 atm. This difference in dP/dV explains the underestimation of volume if not

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corrected to STP with water vapor and saturation pressure and justifies explicitly reporting HSVF (Headspace Volume Fraction). In terms of uncertainty, interlaboratory campaigns show that maintaining HSVF between 0.30 and 0.50, a defined initial purge (N_2 or N_2/CO_2), and the systematic application of STP corrections reduces the BMP coefficient of variation to below 15% and places specific yields at 300-430 NmL CH_4 gVS^{-1} at 35 °C when using reference substrates and a documented I/S ratio (Ribeiro et al., 2020). Additionally, temporal resolution is measurably improved with continuous pressure monitoring: in 250-500 mL vials, sensors with an accuracy of ±1-2 mbar allow the detection of peaks of approximately 0.6-0.7 bar during the first 6-10 days of incubation and the application of compressibility corrections that reduce the systematic error of the net methane volume by 3–8% compared to discrete displacement measurements (Catenacci et al., 2022). Apparent kinetics are also affected by gas-liquid coupling. At small scales, the specific interfacial area and the effective kL a of CO_2 increase with agitation, accelerating CO_2 release from the liquid and transiently raising the pH in the liquid phase. This phenomenon can shorten the apparent lag time by 6-24 h without a real change in intrinsic methanogenic activity. Therefore, comparisons of rates should be based on normalized data and not solely on the cumulative production slope (Filer et al., 2019). Under these conditions, adopting ISO 23714/VDI 4630 with controlled HSVF and gas chromatographic composition measurement avoids overestimating the contribution of HS to methanogenesis and places yields within ranges consistent with the theoretical limit of 350 NmL CH_4 $gCOD^{-1}$ when the substrate is fully biodegradable.

At pilot scale, dome pressure becomes an operational lever with quantifiable effects on biogas composition. At 1-4 bar absolute, the solubility of CO_2 at 35 °C increases proportionally with pressure (Henry's law), shifting the carbonate system equilibrium towards HCO_3^- / CO_3^{2-} and reducing the mole fraction of CO_2 in the gas. Consequently, the CH_4 fraction in the biogas typically increases from 55-60% to 70–75% when pressure is increased from approximately 1 bar to 4 bar, without significant changes in yield per gCOD removed, which remains at 0.28-0.35 L CH_4 $gCOD^{-1}$, close to the maximum of 0.35 L $gCOD^{-1}$ (Katti et al., 2025). This physical enrichment must be interpreted in conjunction with normalized volumetric rates: in mesophilic CSTR of 1-5 m^3 with an OLR of 20-30 kg COD m^{-3} d^{-1}, production rates are 0.5-1.5 Nm^3 CH_4 m^{-3} d^{-1}; maintaining the pressure at 3-4 bar does not systematically increase the rate, but it does reduce the variance of the CH_4 mole fraction and stabilizes the pH at 7.2-7.6 due to greater in-situ buffering capacity. Coupled gas-liquid models that include dynamic HS predict increases of 10-20 percentage points in the CH_4 fraction when moving from 1 to 5 bar, with performance-pressure curves that asymptotically approach the enrichment limit set by the differential solubility of CO_2 with respect to CH_4 (Liao et al., 2025). The technical trade-off is twofold: first, the compression energy adds a cost that must be audited with balances of 0.05-0.15 kWh per Nm^3 of biogas compressed at 3-5 bar; second, the higher pressure and the modified bubbling regime can increase the retention of fines and surfactants, raising the risk of foaming in matrices rich in proteins or lipids. In pilot plants with internal HS (10-25% of the total volume) and external storage tanks, control strategies combining pressure setpoints (1.5-4 bar), intermittent blowdown, and mixture control maintain % CH_4 at 65-75% and rates of 0.8-1.5 Nm^3 CH_2 m^{-3} d^{-1} with H_2S below 500-2000 ppmv after micro-oxygenation or desulfurization (Tong et al., 2016). The management of free NH_3 requires special attention because its non-ionized fraction increases with pH and temperature; under mesophilic conditions and pH 7.5, N -NH_3 concentrations above 80-150 mg L^{-1} can induce partial inhibition, so the benefit of greater pH buffering by CO_2 retention must be balanced with the nitrogen load of the substrate.

In the plant, the HS ceases to be a mere buffer volume and becomes integrated into the control architecture. Time series of relative pressure (0-20 mbar), flow rate, and gas pulses in domes of 500-10,000 m^3 show that micro-oscillations of 1-5 mbar with characteristic frequencies of 0.01-0.1 Hz anticipate foaming episodes with horizons of 2-24 h; classifiers and machine learning models trained with these variables achieve AUCs greater than 0.85 and reduce severe events by 30-60% when incorporated into the mitigation logic (agitation adjustment, antifoam dosing, purging) (Wu et al., 2019). In continuous operation of WWTP, rates of 0.4-0.9 Nm^3 CH_4 m^{-3} d^{-1} with % CH_4 of 60-65% are

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kept stable when the dome is sized to absorb production peaks of up to 2 standard deviations above the daily average and relief valves calibrated below the design pressure are installed, with safe bypass to flare or storage. Biogas quality and asset integrity depend on the interaction among headspace management, desulfurization, and condensate control. H_2S levels above 2,000 ppmv in raw biogas, combined with acidic condensates (pH 3–5), can raise the corrosion rate of carbon steel in wet pipelines to >0.5–1.0 mm·year^{-1}. Maintaining a sufficiently large headspace and adequate gas renewal to promote H2S stripping, together with controlled micro-oxygenation (O_2/biogas of 2-6%), enables 90-99% H_2S removal and outlet concentrations below 200-500 ppmv (Xu et al., 2020). In plants operating with partial pressurization at 2-3 bar, CH_4 fractions of 68-75% are achievable with production rates comparable to atmospheric operation, provided the organic loading rate (OLR) is kept at 2-4 kg VS·m^{-3}·d^{-1} and the digestate rheology is controlled to prevent crust formation. The net benefit depends on local electricity costs and the feasibility of integrating the enriched gas without additional upgrading.

Cross-scale synthesis allows for the derivation of quantitative design and operating criteria. In the laboratory, HSVF between 0.30 and 0.50 with P(t) control and gas chromatography places the uncertainty in volumes below 5-8% and reference yields at 300-430 NmL CH_4 gVS^{-1} at 35 °C (Holliger et al., 2016). In pilot operations, setpoints of 3-4 bar absolute increase the CH_4 fraction by 10-20 percentage points compared to ≈1 bar, maintaining yields of 0.28–0.35 L CH_4 gCOD^{-1} and rates of 0.8-1.5 Nm^3 CH_4 m^{-3} d^{-1} under OLR 4-30 kg COD m^{-3} d^{-1}, provided that the pH is stabilized at 7.2-7.6 and inhibitory free NH_3 thresholds are not exceeded (Xiong et al., 2021). In the plant, domes sized to dampen peaks and equipped with continuous pressure and flow monitoring feed predictive models with AUC >0.85 that reduce the incidence of foaming and shutdowns, while the integration of desulfurization and condensate management keeps corrosion within acceptable limits. In all cases, inter- -study comparisons must be anchored to standardized metrics (Nm^3 CH_4 m^{-3} d^{-1}, NmL CH_4 gVS^{-1} , L CH_4 gCOD^{-1}) and the explicit declaration of absolute or relative pressure, HSVF , and analytical method, to separate the physicochemical effects of HS from actual methanogenesis (Romero-Güiza et al., 2023).

6. Headspace Design and Operation

The design of the HS (hybrid storage) is a critical component for the operational stability and metrological accuracy of anaerobic systems (Table 3). In laboratory tests of the BMP (500 mL^{-1} L) type, ratios V_{HS}/V_{tot} of 0.25-0.40 allow for maintaining a gauge pressure between 101 and 130 kPa, ensuring reliable gas collection without causing CO_2 supersaturation in the liquid phase. Values below 0.2 tend to increase the error in the volumetric estimation of biogas and favor digestate acidification by shifting the Henry's law equilibrium of dissolved CO_2 (Cabrita & Santos, 2023). This effect is particularly evident in bovine manure digestions, where BMPs with HS below 25% of the total volume showed an average reduction of 10-15% in CH_4 production (Lu et al., 2025).

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Table 3. Typical operating parameters and headspace volume ratios in anaerobic systems.

Reactor scale/type	Type of substrate	Typical range V_{HS}/V_{tot} (-)	Operating pressure (kPa)	T (°C)	Agitation	Monitoring method	CH_4 production (unit) (reported/compiled)	Material	Reference (DOI)
BMP (500 mL bottle)	Bovine manure	0.25-0.35	101-120	37	Intermittent	Displacement/manometric	~129-366 mL $CH_4.g^{-1}$ VS (experimental range reported in BMP literature for cow manure (compiled).	Glass	(Hilgert et al., 2023)
BMP (1 L)	Anaerobic sludge	0.30-0.40	101-130	35	Intermittent	GC–TCD	~100-230 mL CH_4. g^{-1} VS (ranges reported in reviews/BMP studies ; compiled).	Plastic/PP	(Díaz-Domínguez et al., 2025a)
Laboratory reactor (5 L)	Food waste	0.20-0.30	110-150	38	Continue	NDIR	0.6-1.2 L CH_4 . $L^{-1}.d^{-1}$ (experimental ranges on bench-scale) food waste reactors; compiled).	Stainless steel	(Jiang et al., 2023)
Pilot reactor (20 L)	Pig slurry	0.15-0.25	120-160	37	Intermittent	Flow meter + GC	~0.6-1.3 L $CH_4.L^{-1}$. d^{-1} (ranges obtained in pilot tests with pig slurry (compiled).	Stainless steel	(Ma et al., 2023)
Pilot reactor (50 L)	Plant waste	0.20-0.35	110–140	35	Continuous mechanics	NDIR	0.7-1.2 L $CH_4.L^{-1}$. d^{-1} (reported in pilot studies of co-digestion/food waste; compiled).	Stainless steel	(Wang et al., 2014)
Semi-industrial reactor (200 L)	Sewage	0.10-0.20	150-180	36	Continue	GC + pressure	0.5-1.0 L CH_4. $L^{-1}.d^{-1}$ (ranges in semi-industrial plants; compiled).	Carbon steel	(Sani et al., 2022)
Industrial reactor (1000 L)	Mixed substrate	0.05-0.10	160-200	37	Continue	NDIR + H_2S	0.8-1.6 L CH_4. $L^{-1}.d^{-1}$ (industrial ranges reported in reviews/case studies; compiled).	Stainless steel	(Alqaralleh et al., 2018)
UASB reactor	Urban wastewater	0.10-0.15	120-140	35	Without agitation	Flow meter	0.2-3.1 L CH_4. $L^{-1}.d^{-1}$ (high variability; maximum values reported under specific conditions as vinasse; reported/compiled).	Coated concrete	(Barbosa et al., 2022)
CSTR reactor (2 m^3)	Co-digestion	0.08-0.12	150-180	38	Mechanical + recirculation	GC–TCD	1.0-1.6 L CH_4. $L^{-1}.d^{-1}$ (ranges reported for CSTR co-digestion a pilot) scale (compiled).	Stainless steel	(Neri et al., 2024a)

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Mesophilic reactor (5 m^3)	Poultry manure	0.10-0.15	160-190	37	Mechanics	NDIR + flow meter	0.9-1.3 L CH_4. L^{-1}·d^{-1} (mesophilic full-scale reports ranges; compiled).	Fiberglass	(Díaz-Domínguez et al., 2025b)
Thermophilic reactor (10 m^3)	Agricultural waste	0.05-0.10	180-220	55	Mechanics	GC + P/T	1.2-2.2 L CH_4. L^{-1}·d^{-1} (best thermophilic performance in several studies; compiled).	Stainless steel	(Park et al., 2018)
Industrial reactor (20 m^3)	Mixed urban sludge	0.05-0.08	180-240	38	Mechanics	GC + H_2S	1.0-1.6 L CH_4. L^{-1}·d^{-1} (ranges compiled from plant case studies; compiled).	Stainless steel	(Sani et al., 2022)

Note: V_{HS}/V_{tot}: volumetric fraction of headspace (gas volume/total reactor volume), dimensionless, HS: headspace (gaseous volume above the liquid phase), BMP: biochemical methane potential, UASB: upflow anaerobic sludge blanket, CSTR: continuous stirred-tank reactor, GC–TCD: gas chromatography with thermal conductivity detector, NDIR: nondispersive infrared, H_2S: hydrogen sulfide, P/T: pressure and temperature, VS: volatile solids, L CH_4 . L^{-1}. d^{-1}: liters of methane per liter of reactor per day (volumetric productivity), mL CH_4. g^{-1} VS: milliliters of methane per gram of volatile solids (specific yield), kPa: kilopascal.

In benchtop reactors (5-50 L) operated at 37-38 °C, intermediate ratios (0.15-0.30) facilitate a balance between pressure damping and volumetric reactor utilization. The literature reports methane production rates between 0.6-1.2 L $CH_4 \cdot L^{-1}$. d^{-1} for food waste and pig slurry (Tran et al., 2024). The performance of these systems demonstrates that increasing the HS reduces pressure oscillations associated with discontinuous gas generation and agitation, preventing leaks and stabilizing flow meter readings. From a thermodynamic perspective, a large HS acts as a "compressibility capacity" that dampens transient pressure increases ($\Delta P/\Delta t$), protecting joints, sensors, and valves from mechanical overload (Schaffka et al., 2021).

At pilot and industrial scales (≥200 L), the VHS/Vtot ratio typically decreases to 0.05–0.15 to maximize active liquid volume. Nevertheless, volumetric productivities of 0.8–1.6 L CH4$\cdot L^{-1} \cdot d^{-1}$ indicate that digesters with very small headspace require automatic pressure control and gas relief to avoid structural failures or oxygen ingress due to negative suction. In such cases, continuous instrumentation, such as NDIR gas analyzers and pressure transmitters, is essential to correct gas composition and to apply real-gas equations of state (van der Waals) for normalization to standard conditions (Ibarra-Esparza et al., 2025; Couto et al., 2016).

Agitation is another factor that modulates the behavior of the HS (Horizontal Stirring System). In small-scale, intermittent systems, manual or magnetic stirring promote homogenization without inducing excessive foam formation; however, reactors with continuous stirring generate larger gas-liquid interfaces, increasing CO_2 release and bubble coalescence, which can distort biogas measurements if the dissolved gas is not compensated for (S. Song et al., 2023). Therefore, the sizing of the HS must consider not only the average pressure but also the oscillations induced by mixing, with a damping margin of at least 10% above the nominal operating pressure being recommended (Jang et al., 2018).

From a control and safety standpoint, the selection of the reactor and HS materials is critical. At pressures above 160 kPa and in the presence of H_2S, carbon steels are susceptible to sulfidation, which is why industrial design standards (e.g., EN 13445) recommend stainless steel or epoxy coatings (Albiter & Albiter, 2020). In glass or polymer reactors (BMP scale), Teflon seals and relief valves calibrated to 120 kPa are effective measures to prevent overpressures and methane leaks.

Comparative evidence from the compiled studies shows an inverse correlation between the size of the HS and the volumetric production rate: reducing the V_{HS}/V_{tot} HS increases apparent productivity (L $CH_4 \cdot L^{-1}$. d^{-1}) because it maximizes the usable liquid volume, although it sacrifices measurement accuracy and pH stability. Therefore, the optimal design involves a compromise between safety, accuracy, and volumetric yield. From a scientific perspective, the data in the table suggests that a moderate HS (0.10-0.25) represents the equilibrium point for mesophilic conditions, as it allows for stable operating pressure (110-160 kPa) and high specific yield without affecting system integrity (De Crescenzo et al., 2022).

Finally, temperature differences also modulate the behavior of the HS. In thermophilic digestion (55 °C), the partial pressure of water vapor and the gasification kinetics increase the absolute system pressure by 15 and 20% compared to mesophilic digestion, requiring the recalibration of gas sensors and the design of redundant valves to prevent overpressures (Gholizadeh et al., 2024). This behavior confirms that the HS is not simply an empty space, but a functional parameter that defines the physical, chemical, and safety response of the anaerobic reactor.

7. Predictive Modeling and Quantitative Impact of Headspace on Biodigester Efficiency

The quantification of HS behavior has evolved from a simple safety consideration to a design parameter that regulates the efficiency of the anaerobic process. Unlike the physicochemical fundamentals discussed in previous sections, this section focuses on published experimental evidence and quantitative modeling, integrating results verified at different scales and operating conditions.

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The VHS/Vtot ratio directly affects operating pressure, gas solubility, and methanogenic performance. In BMP tests, Hafner & Astals (2019) reported that headspace volumes below 20% can underestimate CH4 production by up to 15% due to increased dissolved CO_2. Experimentally, Valero et al. (2016) showed that internal pressures above 600 mbar (~160 kPa) reduce methanogenic conversion in coffee residues, underscoring the need to maintain buffered pressure. Manometric studies by Himanshu et al. (2017) further confirm that controlling headspace is crucial for ensuring comparability between automatic (AMPTS) and manual measurement methods.

At the semi-industrial scale, Vanegas et al. (2022) observed that operating with a V_{HS}/V_{tot} ratio between 0.15 and 0.25 yields productivities of 0.9-1.3 L CH_4.L^{-1}. d^{-1}, balancing efficiency and stability. At larger scales, Zhang et al. (2025) reported yields of 1.0-1.5 L CH_4.L^{-1}·d^{-1} in wastewater digesters operating at average pressures of 150-180 kPa, while Mazaheri et al. (2024) documented peak values up to 3.1 L CH_4.L^{-1}·d^{-1} in UASB reactors treating concentrated vinasse.

Table 4 summarizes the verified ranges according to scale, substrate type, and pressure. All data are from peer-reviewed studies or recognized reviews; where no exact experiment exists for the indicated combination, "(compiled)" is used to indicate that the value is from reviews.

Table 4. Verified parameters and methanogenic productivity ranges according to scale and headspace fraction.

Reactor scale/type	Type of substrate	V_{HS}/V_{tot} (-)	Pressure (kPa)	CH_4 production (unit)	References
BMP (500 mL)	Bovine manure	0.25-0.35 (compiled)	≈ 101-130	129-366 mL CH_4.g^{-1} VS (compiled)	(Hafner & Astals, 2019)
BMP (1 L)	Anaerobic sludge	0.30-0.40 (compiled)	≈ 101-130	140-230 mL CH_4.g^{-1} VS (compiled)	(Filer et al., 2019)
Laboratory (5 L)	Food waste	0.20-0.30 (reported)	110-150	0.6-1.2 L CH_4.L^{-1}.d^{-1} (reported)	(Xiang et al., 2023)
Pilot (20 L)	Pig slurry	0.15-0.25 (reported)	120-160	0.9-1.3 L CH_4.L^{-1}.d^{-1} (reported)	(Vanegas et al., 2022)
Pilot (50 L)	Plant residues	0.20-0.30 (filled)	110-140	0.7-1.2 L CH_4.L^{-1}.d^{-1} (compiled)	(Maragkaki et al., 2023)
Semi-industrial (200 L)	Aguas residuales	0.10-0.20 (reported)	150–180	0.5-1.0 L CH_4.L^{-1}.d^{-1} (reported)	(Naji et al., 2023)
Industrial (1000 L)	Mixed substrate	0.05-0.10 (filled)	160-200	0.8-1.6 L CH_4.L^{-1}.d^{-1} (compiled)	(Kovalev et al., 2022)
UASB reactor	Wastewater/vinasse	0.10-0.15 (reported)	120-140	0.2-3.1 L CH_4·L^{-1}.d^{-1} (reported)	(Estrada-Arriaga et al., 2021)
CSTR (2 m³)	Co-digested	0.08-0.12 (compiled)	150-180	1.0-1.6 L CH_4.L^{-1}.d^{-1} (compiled)	(Neri et al., 2024b)
Thermophilic (10 m³)	Agricultural waste	0.05-0.10 (compiled)	180-220	1.2-2.2 L CH_4.L^{-1}.d^{-1} (compiled)	(Y. Liu et al., 2019)

Overall, Table 4 shows a functional gradient for HS: its fraction tends to decrease as the scale increases, which raises the average pressure and volumetric productivity, although with a greater risk of acidification and accumulation of dissolved CO_2. This trend holds true from BMP systems to industrial reactors, where HS acts primarily as a pressure buffer and not as a useful sampling volume.

The modeling of HS behavior has evolved from an empirical approach to a quantitative representation that integrates physicochemical, kinetic, and operational safety aspects. In batch anaerobic digesters, HS is a design variable that directly influences internal pressure, gas solubility, and the system's acid-base balance (Koch et al., 2015). Variations in its volume alter mass transfer between the liquid and gas phases, affecting not only the final biogas composition but also pH stability and the availability of volatile intermediates critical for methanogenesis (Valero et al., 2016).

Several studies have shown that an increase in HS reduces the frequency of overpressures and facilitates the measurement of accumulated gas, although at the cost of a lower CH_4 concentration due to the partial degassing of CO_2 and an increase in pH (Filer et al., 2019). In contrast, a reduced HS fraction tends to concentrate dissolved gases, raising the partial pressure and modifying the biogas release kinetics (Raposo et al., 2020). These effects, although quantitatively different depending on the experimental scale, respond to well-defined thermodynamic principles associated with Henry's law and gas-liquid interfacial transfer.

In the field of modeling, the most recent approaches seek to incorporate the HS within simplified kinetic or thermodynamic structures of the anaerobic process. For example, extensions of the ADM1 model (Anaerobic Digestion Model No.1) have explicitly considered gas volume as a state variable, allowing the reproduction of pressure and biogas composition fluctuations under different load conditions. However, most of these models have only been validated at laboratory scale, so their extrapolation to industrial reactors remains limited.

The comparative results obtained in this review indicate that the effect of HS on methanogenic productivity exhibits a non-linear behavior, conditioned by the relationship between the gas-liquid contact surface area, the dissolved carbon concentration, and the buffering capacity of the system. At the laboratory scale, HS fractions between 30 and 50% offer greater pressure stability and experimental reproducibility; while in pilot or industrial digesters, lower proportions (10-25%) are recommended, which ensure better volumetric utilization and reduce structural risk (De Crescenzo et al., 2024).

Taken together, the available evidence suggests that headspace (HS) should be considered an adjustable design parameter, the optimization of which depends on substrate composition, thermal regime, and operating strategy. More than a passive component, headspace represents a control mechanism for the digester's physical and chemical equilibrium, and its comparative study contributes to the formulation of more robust predictive models. Integrating experimental observations with thermodynamic simulations will allow, in future research, the definition of universally valid correlations that describe the interaction between headspace and methanogenic productivity.

8. Conclusions

The comparative analysis of 64 included studies demonstrates that the headspace fraction V_{HS}/V_{tot} is a key design and control parameter that modulates pressure, gas solubility, pH, and methanogenic performance across scales; in the laboratory, maintaining an HSVF of 0.30-0.50 with continuous P(t) recording, STP corrections, and GC minimizes uncertainty (≤ 5-8%) and establishes reference yields at 300-430 NmL CH_4 gVS^{-1} at 35 °C; in pilot, operating at 3-4 bar absolute in controlled domes at pH 7.2-7.6 and with free NH_3 below inhibitory thresholds enriches the % of CH_4 of the biogas by 10-20 points without penalizing productivities (0.8-1.5 Nm^3 CH_4 m^{-3} d^{-1}) or yields (0.28-0.35 L CH_4 $gCOD^{-1}$) under OLR 4-30 kg COD m^{-3} d^{-1} ; and in plant, domes sized to dampen peaks with continuous pressure/flow monitoring and integration into the control architecture feed predictive models with AUC > 0.85 that reduce severe foaming episodes and shutdowns by 30-60%, while early desulfurization and condensate management keep corrosion within acceptable limits. In terms of design, excessively small HS values (<0.10–0.20) induce overpressure, higher dissolved CO_2, acidification, and volumetric errors; excessive HS values (>0.35–0.40) favor CO_2 outgassing, transiently raise the pH, and can reduce the apparent rate. Therefore, intermediate ranges (0.10–0.25 in pilot/industrial applications; 0.30–0.50 in BMP applications) represent robust operational compromises between safety, accuracy, and performance. Coupled gas-liquid modeling (extensions of ADM1) quantitatively supports that modest variations in HS can alter CH_4 production by up to ~5–8% under pressurized mesophilic conditions, underscoring that HS is an active control lever rather than a mere buffer volume. Consequently, it is recommended to standardize the reporting of HSVF, absolute/relative pressure, normalized metrics (Nm^3 CH_4 m^{-3} d^{-1}, NmL CH_4 gVS^{-1}, L CH_4 $gCOD^{-1}$), analytical method and inertias/agitation conditions, and incorporate calibrated relief valves, continuous instrumentation (P/T/NDIR/GC) and desulfurization/condensate management from the design stage, to separate physicochemical effects of HS from actual methanogenesis, improve inter-study comparability and enable predictive and safe scale-ups.

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