

Enhancing Methane Yield via Biomethanation and Kinetic Modelling.

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Abstract – This investigation explores the enhancement of CH₄ generation in anaerobic digesters (AD) via in-situ renewable hydrogen injection utilising four exotic crop wastes and a crop (five feedstocks). The substrates are yam, cassava, and cocoyam peel (YP, CP and CYP), rice husk (RH) and finger millet seeds (FMS). Biomethane Potential (BMP) Tests, followed by AD experiments with food waste inoculum (FWI), were conducted in triplicate under mesophilic conditions (37°C), utilising an anaerobic model (ANM) test rig. The last phase of the experimental campaign is bio-methanation to upgrade CH₄ purity. CYP and YP showed 233% and 81.5% higher gas yields, respectively, with CH₄ content improvements up to 38.5%. However, CP emerged as the optimal feedstock, hence the primary substrate utilised in the AD, supporting hydrogenotrophic methanogenesis (HM) and CO₂ to CH₄ conversion. Consequently, MATLAB-based kinetic modelling confirmed the Richard equation as the best fit predictor. The novelty of this study lies in the innovative incorporation of in-situ H₂ injection (0.67 ml/min), bubble mixing and mass transfer to enhance CH₄ from tropical crop waste (cassava peel), a widely available yet underutilised feedstock specific to Plateau State, Nigeria. Additionally, integrating computational fluid dynamics (CFD) and bioprocess kinetic modelling provides a comprehensive framework for understanding the parameterisation and optimising system dynamics. This consolidates the research contribution to the experimental optimisation of decentralised biogas systems, facilitating sustainable energy solutions for pipeline quality in tropical regions.

Keywords: Feedstock BMP characterisation, in-situ renewable hydrogen injection, transport phenomena, kinetic modelling and Plateau State, Nigeria.

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1. Introduction

The rising worldwide energy requirement and growing waste generation due to massive population growth have necessitated extensive research in renewable and sustainable energy systems. This energy system has become imperative as a solution to the rising energy demand. AD seems to be a veritable pathway, considering the overexploitation of fossil fuels and accelerated energy demand. Both are responsible for the substantial decrease in fossil fuel abundance in the Earth's natural reserves [1]. Unlike fossil fuels, biomass energy conversion requires limited technical, cost, accessibility demands and environmentally friendly [2]. The bioenergy can be utilised for electricity/heating and refined to meet pipeline-quality fuel standards [3][4].

In developing nations such as Nigeria, where agricultural wastes are plentiful, crop processing waste, decayed crops due to insufficient storage facilities, disease-infected crops, and crops affected by pest infestations are also included [5]. AD holds significant potential for decentralised energy generation [6].

However, CH₄ yield, and purity limitations often restrict biogas systems from achieving full energy recovery and integration into established energy networks. The composition of biogas comprises CH₄ and CO₂, ranging from 55 to 65% and 45 to 35%, respectively, along with trace gases such as hydrogen sulphide (H₂S), constituting between 0.1% and 3% and ammonia (NH₃) [1]. One of the primary issues in this fraction is the incomplete conversion of CO₂. Recent investigations have shown the potential H₂ assisted pathway to augment CH₄ production. This method uses H₂ to directly convert CO₂ into CH₄ within the digester, providing a cost-effective solution for biogas enhancement while preserving anaerobic stability. Similarly, challenges like poor gas-liquid mass transfer and mixing dynamics hold back the scalability of this process [7].

As a result, this investigation explores five commonly consumed exotic crops peculiar to Plateau State, Nigeria. These feedstocks include CP, CYP, YP, RH, and FMS, which were selected based on availability, composition, and relevance to local consumption patterns. The study applies a three-phase experimental campaign, combining BMP testing, standard AD, and bio-methanation. Consequently, a parametric comparative kinetic modelling and a fluid-thermal analysis framework were followed to examine gas mixing, thermal control, and mass transport. The novelty lies in coupling kinetic analysis with momentum, heat, and mass transport assessments to understand their parameterisation and optimise system dynamics. Bridging the gap by integrating experimental findings with MATLAB-based modelling and transport phenomenon analysis. Fundamentally, to develop a practical, scalable framework for improving CH₄ yield and biogas purity. The results analysis will help to facilitate sustainable energy policies, waste valorisation methods, and decentralised bioenergy planning across government, academic, and industry sectors.

2. Related Work

2.1. Feedstock Suitability and Energy Recovery from Crop Waste

Nigeria's agricultural sector produces many exotic crop residues that remain largely untapped for renewable energy recovery. These wastes are readily available for energy generation sources via combustion,

pyrolysis and AD [8] [6]. Nigeria is typically a foremost global producer of tuber crops, including cassava (approximately ~ 63 Mt/yr.) [9] [10] cocoyam (~2.7 Mt/yr.), yam (~45 Mt/yr.) [11], as well as cereals; rice (82 Mt/yr.) [12] and finger millet (1.5 Mt/yr.) [13]. These feedstocks have differing biochemical characteristics, which influence their biodegradability, energy yield, and process kinetics during AD. The abundance of these high-energy crops, with typical Low Heating Value (LHV) of 16.4, 16.43, 16.43, 16.4, and 15.4 MJ/kg for cassava, cocoyam, yam, rice and finger millet, respectively [14], making their respective generated waste a potential source of bioenergy.

Typically amount of waste, i.e. cassava (~37.8 Mt/yr.), cocoyam (~1.7 Mt/yr.), yam (~2.9 Mt/yr.) peels, rice husk (~2.6 Mt/yr.) and finger millet straw (2.2 Mt/yr.) are produced with a corresponding energy content of 10.61, 14.24, 16.4, 16.02 and 15.4 MJ/kg [15] [6]. Oguntoké et al. earlier reported that 82 Mt/yr of crop waste, with a biogas estimate of ~4.98 billion m³/yr, can be used to generate 117,000 TJ/yr of energy [5].

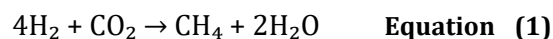
2.2 Lignocellulosic Feedstock Limitations and Energy Recovery

Lignocellulosic biomass, like RH and FMS, presents a very high energy potential, limited by poor hydrolysis and high fibre content, which limits degradability. The biochemical resistance of the Lignocellulosic Fraction poses a significant hurdle in AD [16]. This result aligns with the current findings, where feedstocks like RH showed delayed and reduced methane output, necessitating pre-treatment or co-digestion strategies for enhanced performance [17], [18], [19]. CP valorisation showed its potential as a value-added product source beyond simple waste treatment [19].

2.3. In-Situ Hydrogen Injection and Hydrogenotrophic Methanogenesis (HM)

Bio-methanation in the upgradation of methane in anaerobic systems offers a compelling route by consuming CO₂ to CH₄ via HM and AM (Acetoplastic Methanogenesis) [1]. It has also been reported that enriching hydrogenotrophic methanogens like *Methanothermobacter*, can utilise H₂ and CO₂ directly to boost CH₄ purity [21], [22]. The prevalence of AM (*Methanosarcina*) and HM (*Methanobacterium*) species is contingent upon the substrate utilised in AD. Regarding thermodynamic stability, the HM pathway is

more advantageous than the AM pathway [1]. Their stoichiometry HM converts 1 mole of CO₂ and 4 moles of H₂ into 1 mole of CH₄, as expounded by Lai et al. [21]. The AD HM route accounts for up to 30% of the CH₄ content in biogas composition, with reduced H₂ concentration [1].



Recent studies show bio-methanation significantly improves CH₄ content by stimulating HM [20], [26]. It was also demonstrated that recirculating gases and supplying H₂ in methanogenic reactors enhance CO₂-to-CH₄ conversion[21]. However, H₂ mass transfer limitations and microbial inhibition at high partial pressures remain a significant challenge [26]. Some in-situ biogas upgradation techniques were also reviewed in another study, highlighting the need for optimised H₂ dispersion to prevent energy losses [23].

2.4. Role of Mass and Momentum Transfer

The crux and the innovation in this investigation is the integration of bubble-induced mixing, microbial uptake efficiency, and thermal dynamics within the AD systems on exotic crop waste peculiar to Plateau State, Nigeria. Computational Fluid Dynamics (CFD) based modelling was used to buttress bubble behaviour and interfacial area optimisation to boost H₂ solubility and microbial accessibility [1], [24]. Properly comprehending bubble dynamics, mixing substrate, and microorganism interactions is key to optimising reactor performance. This is a state-of-the-art review of gas absorption using CFD modelling to explain vividly how the transport process governs conversion efficiency. In anaerobic systems, poor hydrogen dispersion can limit microbial access, reducing methane production efficiency, as observed in this experiment.

Understanding this process is necessary, considering the mass transfer mechanism and dynamism in moist biomass systems with peels and pulp-based feedstocks [23]. This investigation also confirms how biogas affects mixing efficiency. Therefore, overcoming mass transfer barriers using microbubble diffusion techniques can further inform and improve future reactor design refinements for this kind of system, as observed in this experiment[23].

2.5. Kinetic Modelling for Predictive Optimisation

As the best-fitting kinetic expression, Richard's model demonstrates an advanced approach to modelling dynamic typical digestion behaviour. This expression aligns with the growing body of literature supporting non-linear models like Gompertz, Richards over simple first-order kinetics, especially when accounting for lag phases, multi-phase transitions and microbial adaptation [23], [25]. The MATLAB-based kinetic simulation in this investigation concretises mass transfer coefficients and microbial growth constant. Integrating explicit physical transport parameters and biological uptake

2.6. Towards Pipeline-Quality Methane and Decentralised Energy

The research capability's reaching 75% CH₄ purity without complete CO₂ removal confirms the possibility of AD as a probable energy generation system in Nigeria. Considering the strategic alignment of feedstock selection/characterisation, transport mechanism and microbial targeting is a precise gradation to the possibility towards a local, decentralised biogas solution. The residual CO₂ fundamentally limits energy density, showcasing onsite calorific value upgrading of (~22 MJ/m³) [26]. This innovative study bridges the gap by showcasing a scalable H₂ Injection model under mesophilic conditions.

However, advances in bio-methanation and CFD modelling [21], [7] demonstrate the technical feasibility of producing pipeline-quality CH₄ ≥ 90% from exotic crop waste. Plateau State accounts for over 1.2 million tons/year of cassava and RH waste [16]. The absence of BMP standards in the National Renewable Energy Policy (NREP, 2015) creates a critical adoption barrier. Consequently, the evidence of HM achieving CH₄ purity of ≥ 95% is visible as far as:

- Policy-driven incentives like feed-in tariffs for cleaned biogas are available
- Modular upgrading systems (e.g., membrane separation and pressure swing adsorption for decentralised use are also available [26].

Though the kinetic models optimise CH₄ yield performance, the knowledge gap is their scalability contingent on state-level energy planning. Few studies in West Africa have examined how government policies can help decentralised small-scale biogas systems, especially in Plateau State, for high-quality and efficient methane generation.

3. Materials and methods

3.1. Biomethane Potential (BMP) Test

Phase I incorporate BMP testing on four waste-derived samples (YP, CP, CYP, and RH) and one newly discovered crop, finger millet seeds (FMS), sourced from Plateau State, Nigeria. While waste-based feedstocks were analysed, FMS was included to evaluate its potential as an energy crop before considering its waste for future studies. Figure 1 shows three crops and their waste components, RH and FMS. 500 g of all feedstocks were transported to NRM Laboratories (Bracknell) for characterisation. Samples were dried, ground, and characterised for proximate and ultimate analysis. Their respective theoretical bio-methane potential and volatile solids (VS) were also determined. Characterisation was defined using standard methods for analytical chemistry procedures, also known as physicochemical properties (PP).



Figure. 1: Exotic Feedstocks and their waste component cultivated in Plateau State, Nigeria.

3.2. Anaerobic Digestion (AD)

Phase II involves inoculum preparation, feedstock sourcing/preparation, and AD experimentation. Food waste inoculum (FWI) was utilised for the experimentation, extracted from a food waste biodigester in the Celignis laboratory, and stored in a 30° C incubator. It was degassed under mesophilic conditions (37 ° C) for a week before utilisation. Feedstocks were injected in wet conditions, and the inoculum was used after 5 days of collection. 3.2 g each was collected from CP, CYP, and YP, 4.45 g for RH and 4.2 g for FMS. FMS was pounded, RH was milled, and the husk was collected (see Figure 1). FMS, RH, CP, CYP, and YP substrates were tested in 1 L (1000 ml) batch digesters known as the Anaero Nautilus Bioreactors (ANB) (see figure 2) at 37°C and 1 atm. The experiment

followed the VDI 4630 (2016) standards protocols, with an inoculum-to-substrate ratio (ISR) of 4:1 on a volatile solid (VS) basis. The experiments were conducted in triplicate. ANB consist of fifteen one-litre containers, but only 700ml is actively used, fully immersed in the Nautilus water bath with a tight water cover, reducing evaporation. The system was continuously shaking to maintain and simulate semi-continuous operations. Energy balance calculations were performed to assess the net energy gain, while the theoretical methane yield was benchmarked at 374 L/kg VS.



Figure. 2: The test rig utilised is the Anaero Nautilus Model @ Mesophilic (37° C)

3.3. In-situ Renewable Hydrogen Injection

Phase III involved bio-methanation. H₂ generated by renewably powered electrolysis is forcefully broken down from water molecules through electrolysis, collected, stored, and injected in situ directly during the AD. H₂ mass flow rate was continuously injected at 0.67ml/min and introduced through a porous diffuser at a stoichiometry ratio of H₂: CO₂ = 4:1 (see equation 1). Operating conditions remained 1 atm in mesophilic conditions (37 ° C). HM were enriched to boost metabolic activity. Gas chromatography (GC) analyses of CH₄ and CO₂ were calibrated while CH₄ content, total biogas volume, and pH were monitored daily. Kinetic modelling was done using three models: First-order, modified Gompertz, and Richards. Parameters such as lag phase, maximum methane production rate, and ultimate methane yield were estimated. Mass and heat transfer analysis included bubble dispersion patterns and microbial uptake assumptions, drawing from validated parameters in the literature.

4. Results and Discussion

4.1. Feedstock Characterisation

As shown in Table 1, FMS exhibited the highest VS/TS ratio of 97%, and a gas yield of 470 L/kg VS, indicating superior biodegradability. RH shows slower degradation

due to a high % fibre content of 47% [27], though it is high in TS with 94%. Moist feedstocks like CP, CYP, and YP may reduce water demands but pose viscosity risks [19]. CP has the highest CH₄ purity of 57.3%, making it a strong candidate for energy recovery despite a lower total yield (174 L/kg VS). However, these properties influence mass and heat transfer in degradability [24] based on their significant digestibility and momentum via mixing efficiency during reaction.

Table 1: Nutrient composition and BMP test of feedstock

Feedstock/properties	RH	FMS	CP	CYP	YP
Volatile Solids (%)	74.6	85.3	28	22.4	34.3
Total Solids (%)	94.0	87.8	29.3	24.5	36.6
Crude Protein (%)	2.8	8.7	2.4	2.4	3.3
Crude Fibre (%)	47.0	5.5	2.3	2.7	2.4
Moisture %	6.0	12.2	70.7	75.5	63.4
Ash (%)	19.4	2.5	1.3	2.1	2.3
Oil-B (%)	0.5	1.8	6.9	0.4	0.4
NFE	24.3	69.3	16.4	16.9	28.2
Oven Dry Matter (%)	94.0	87.8	29.3	24.5	36.6
VS/TS	79.4	97.2	95.6	91.4	93.8
Total Gas Yield (l/kg VS)	427	470	174	124	189
Total methane content (%)	51	52	57.3	52.4	52

4.2. Anaerobic Digestion

Phase two is the AD. The analysis of Table 2 revealed that CP, CYP and YP had substantial CH₄ increase from +17.7 % to +20%. CYP showed significant improvement, having 413 L/kg VS (+233% gas yield). However, these properties, influence mass and heat transfer in

highlighting the role of pre-treatment in enhancing biodegradability in optimising AD outcomes. CP, YP and CYP had the highest post-AD CH₄ content of 75% and 72%, respectively, with CYP achieving a +19.6% increase. FMS and RH had reduced gas yields (-43.6% and -39.3%) but modest CH₄ increases of +7% and +4%, indicating less efficient substrate utilisation without pre-treatment. Figure 3 shows a CYP of 413, and a YP of 343 L/kg VS. However, higher CH₄ content, especially in CYP and YP, signifies greater energy density by improving thermal efficiency. Considering C/N ratios, maintaining an optimal level of 20:1 and 30:1 is crucial to promoting stable microbial activity, while also preventing ammonia/acid toxicity and enhancing CH₄ yield performance[16], [19].

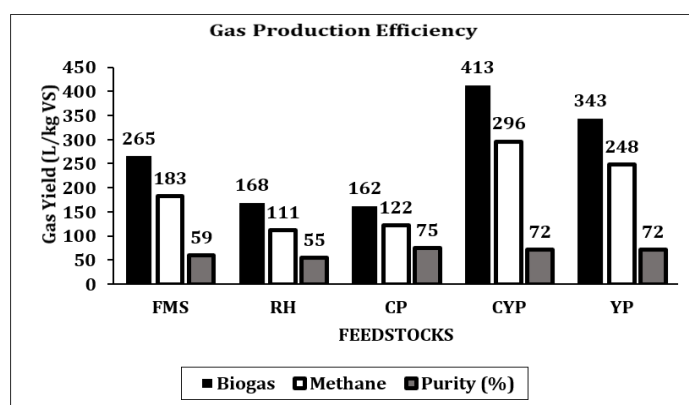


Figure. 3: Comparative Results on Biogas, Biomethane and Purity Across Feedstocks with RH – Rice Husk, FMS – Finger Millet, CP – Cassava Peel, CYP – Cocoyam Peel, YP – Yam Peel

Table 2. Comparative Biogas and Methane Production Performance of Feedstocks. Gas yield (L/kg VS) Percentages in Parentheses indicate changes relative to baseline conditions*

Feedstocks	Gas Yield (L/kg VS)	CH ₄ Increase	Initial CH ₄ (%)	Post AD CH ₄ (%) Increase
FMS	265 (-43.6%)	183 (+13.5%)	52	59 (+7)
RH	168 (-39.3%)	111 (+78.5%)	51	55 (+4)
CP	162 (-6.9%)	122 (+30.9%)	57.3	75 (+17.7)
CYP	413 (+233%)	296 (+37.4%)	52.4	72 (+19.6)
YP	343 (+81.5%)	248 (+38.5%)	52	72 (+20)

CH₄ increase, signifying effective methanogenesis. Consequently, if the C/N is unbalanced, co-digestion or feedstock adjustments are necessary for smooth AD. All tested feedstocks (TBF) achieved >70% CH₄ content, nearing pipeline-grade quality (>80% CH₄), confirming in-situ upgrading potential [26]. CYP and YP achieved the most significant CH₄ enrichment rates at +37.4% and +38.5%. CP achieved a steep increase in CH₄ yield by +30.9% after experiencing a 7-day lag phase because of cyanogenic glycosides. Biogas with increased CH₄ content exhibits approximately 50% more energy density than untreated biogas. Figure 4 demonstrates that CYP achieved the maximum biogas production at

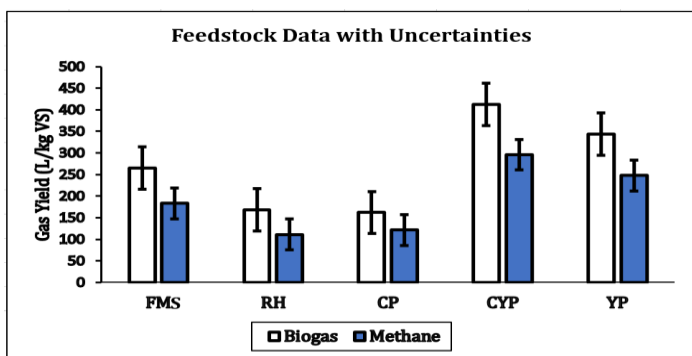


Figure 4. Biogas and Methane Generation with Variabilities Across Feedstocks with error bars representing ± 1 standard deviation.

413 ± 27 L/kg VS and the highest biomethane output at 296 ± 19 L/kg VS. This is the best for gas production and the most energy-rich gas production. YP is second, while CP is the most reliable, but the lower-yield FMS has high variability. Figures 5 and 6 showed that FMS achieved the fastest production start on Day 1 but produced the lowest CH_4 upgrade at +13.5%, persisting throughout the entire 28th day with a yield of 265 L/kg VS. Furthermore, Figure 6 shows the corresponding

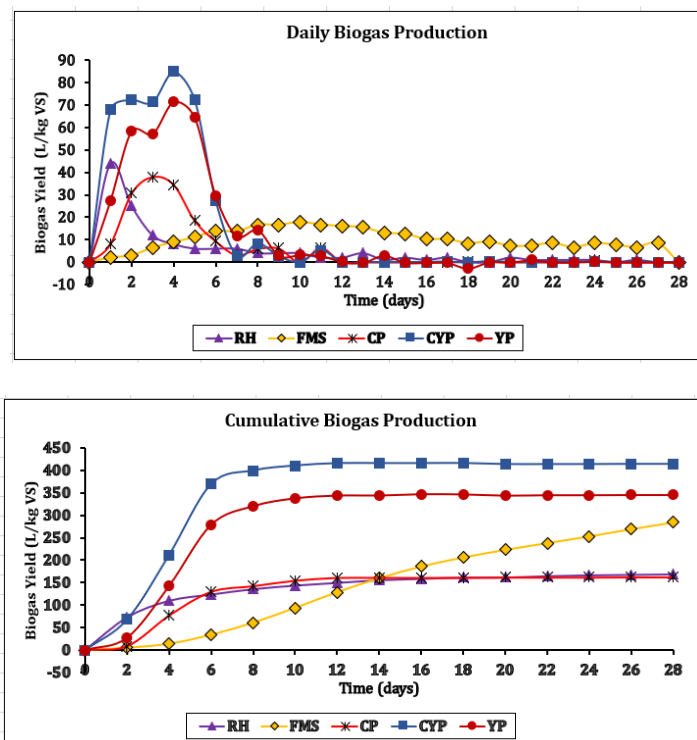


Figure 5. Daily and Cumulative biogas production curves of exotic feedstock with RH – Rice Husk, FMS – Finger Millet, CP – Cassava Peel, CYP – Cocoyam Peel, YP – Yam Peel (means with error bars indicating triplicate values).

transient biomethane production, except for CP, experienced a 7-day lag period before increasing production until 15 days. CP started on the 8th day. The delay in CP may be because of high amounts of cyanogenic glycosides. The seven-day lag phase led to a quick overall yield due to significant microbial growth during the log phase, which lasted from days 8 to 13. This was followed by minimal biogas production in the death phase on the 14th and 15th days. RH and CP showed moderate yields but distinct kinetics. Key kinetics analysis shows that 80–92% of total biogas peak production occurred between Days 6–19 for most feedstocks. CP's 7-day lag preceded rapid methanogenesis from Days 8 to 15, likely due to microbial adaptation. CYP and YP achieved >95% total production within 15 days, and FMS yield performance from Day 1, with CP's highest purity of 75% CH_4 showing

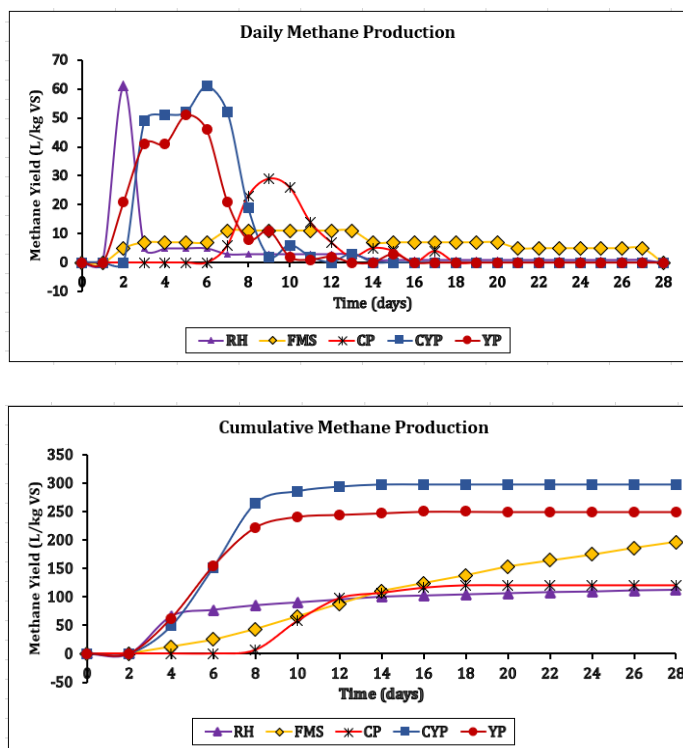


Figure 6. Daily and Cumulative methane production curves of exotic feedstock with RH – Rice Husk, FMS – Finger Millet, CP – Cassava Peel, CYP – Cocoyam Peel, YP – Yam Peel (means with error bars indicating triplicate values)

process efficiency. However, CYP/YP balanced high yield of >300 L/kg VS) and upgrading potential (+37–38% CH_4) shows both process efficiency and feedstock suitability. However, RH underperformed due to a slower degradation peak on Day 26 and stopped

producing, achieving a total volume of 168 L/kg VS. Feedstock selection critically impacts production timelines and CH₄ quality. In-situ hydrogen injection could optimise CP and CYP/YP outcomes. However, CP was chosen for the in-situ bio-methanation because of its highest BMP test value.

4.3. In-situ Renewable Hydrogen Injection

The conversion gradation of AD consists of four stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Nevertheless, methane production during the four stages can occur through acetoclastic methanogenesis (AM) and hydrogenotrophic methanogenesis (HM). Thus, syntrophic activity between AM and HM must coexist inside the reactor to achieve higher CH₄ content in the biogas composition through bio-methanation [1]. Similarly, H₂ was introduced into the AD system to consume CO₂ to produce more CH₄, enhancing methane purity to a Natural Gas Standard of above 90%, the crux of this investigation [28].

Bio-methanation requires bubble movement within the AD system, essential for facilitating microbial interaction with the substrate. Gas-induced mixing is necessary to increase CH₄ levels. Consequently, the significant advancements we observe improve heat exchange, reduce mixing energy, and improve mass transfer in biogas systems. This experiment utilised an advanced test rig, the Anaero Nautilus model (ANM), to optimise technical performance driven by a gearbox for consistent mixing. Recent studies have shown that hydrogen bubbling can boost mass transfer, which in turn helps microbes absorb more by overcoming solubility limits[24], [28]. Figure 7 illustrates a notable

rise in CH₄ and total biogas, especially between Days 1 and 14, signifying vigorous microbial fermentation. From the 16th to the 28th day, the yield performance steadied, indicating that microbial activity may have attained maximal efficiency [16], [21], [27]. This unique process demonstrated a significant boost in conversion efficiency in reducing CO₂, the impact of H₂, and the evidence of increased CH₄ yield, especially during methanogenesis when the ultimate HM routes were essential. The shift in the biogas composition was very explicit, confirming yield efficiency.

By introducing H₂, the lag phase was significantly reduced, thanks to an earlier surge in microbial activity during digestion [6], [28]. This led to a faster increase in biogas production, while the purity remained steady. Figure 7 illustrates how improved breakdown of lignocellulosic materials in CP resulted in more efficient substrate utilisation and higher overall gas yields. This is crucial for converting complex carbohydrates into simpler molecules that are more responsive to fermentation [29], [30].

Better mixing can improve gas-liquid interaction by creating the conversion gradient of AD. Nevertheless, methane production during the four conversion stages can occur through acetoclastic methanogenesis (AM) and hydrogenotrophic methanogenesis (HM). Thus, syntrophic activity between AM and HM must coexist inside the reactor to achieve a higher CH₄ content in the biogas composition.

We can also improve Gas-liquid interaction by creating smaller bubbles to increase biogas efficiency in the systems [7], [22], [23].

The assay's Hydrogen equivalent injection mass flow calculation on the molar ratio stoichiometry in the balanced chemical equation was 0.67 ml/min. Due to the incomplete chemical bonding between H₂ and CO₂, the quality dropped from 75% to 51.6%, a relative reduction of 31.2% and an absolute drop of 23.4%, according to a volumetric analysis. This task encompasses technological problems such as managing, stabilising processes, key performance metrics and manipulating specific microbial pathways during biogas generation. The good news is that biogas increased from 162 to 329 L/kg of VS and biomethane from 120 to 252 L/kg of VS. Biogas and biomethane increased by 101.8% and 110%. Consequently, even with some CO₂ conversion, we could not reach full methanation due to the reactor's design and microbial population limitations. While bubbles' movement affects how bacteria engage with substrates, we still need a small quantity of extra gas-induced

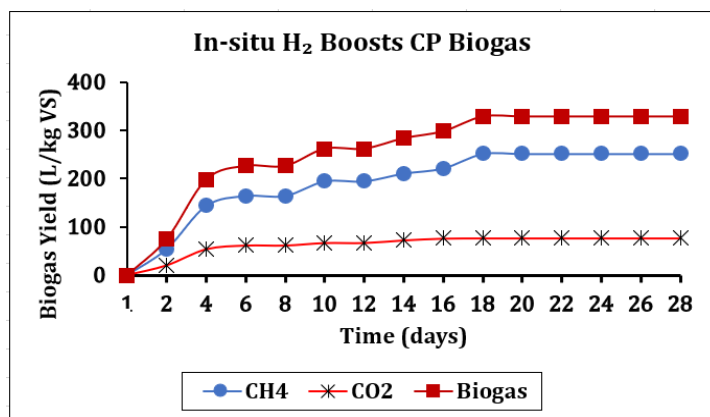


Figure 7. Biogas Generation of Cassava Peel (CP) with the effect of In-situ Hydrogen Injection.

mixing to ramp up CH₄ production. This noteworthy improvement implies that we may significantly enhance CH₄ quality and raise the efficiency of biogas systems by improving heat exchange and mass transfer while lowering mixing energy [7], [22] [23].

4.4. Comparative Analysis with and without H₂

4.4.1. Biogas Composition without H₂

Figure 8a showed the AD without H₂ direct input, the CO₂/CH₄ ratio of baseline digestions, as shown with the red line (CO₂) an intriguing trend initially greater than the blue (CH₄), which shifted from the right to the left on the 10th day, gradually falling below the blue line until the 28th day, indicating a predominant acidogenic but low methanogenesis phase. The sharp rise shows a slow hydrolysis reaction, with high CO₂ peaking at almost 60% of the total biogas composition during the initial 10 days due to acidogenic methanogenesis. The 7-day lag phase observed impacts overall productivity, with CH₄ output beginning to increase only after the seventh day. This suggests that without H₂, the system struggled to achieve optimal methanogenic activity. H₂ derived from lignocellulosic breakdown [24], [16] is highly responsible for the strong native hydrogenotrophic archaea (Methanothermobacter) [21], [20], impacting high CH₄ purity of 75% from the 8th to the 28th day. The rise mirrors fibre-rich feedstock behaviour [16], [20], and the subsequent surge suggests mediated CO₂ conversion [26].

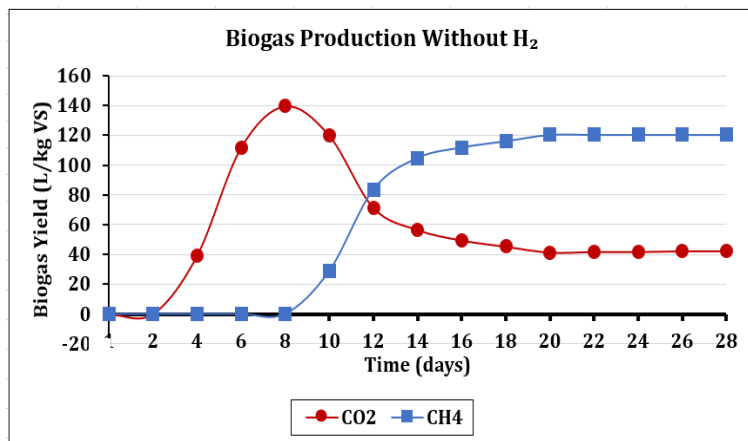
4.4.2. Biogas Composition with H₂ Input

Conversely, when H₂ was introduced to AD, as shown in Figure 8b, the blue line was above the red line, demonstrating in-situ CO₂ sequestration via HM, offering a promising future research and application outlook. Here, the red line (CO₂) consistently remained below the blue line, signifying that the high-powered H₂ has humbled the red line, improving biogas dynamics and conversion efficiency [1], [21]. A remarkable increase in microbial activity drove a more effective hydrogenotrophic conversion. The result was a significant increase in biogas density, with the dynamics shifting from a CO₂ state to a balanced state until the 28th day.

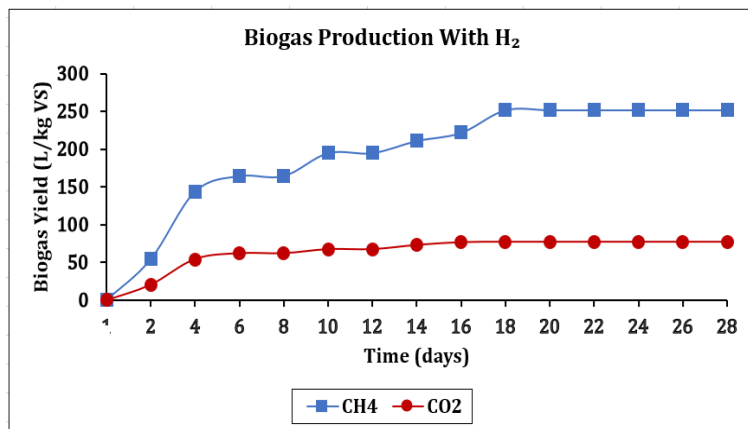
4.4.3. Mechanism of Improvement

The analytical data reveal significant insights into microbial activity and substrate dynamics of H₂ and CO₂ interplay in CH₄ generation. Comparing Figure 8a and 8b, H₂ injection reversed the CO₂/CH₄ baseline digestion

ratio from Figure 8a, where the red line is above the blue line, to Figure 8b, where the blue line is above the red line, demonstrating in-situ production efficiency. Insights from chemical reactor studies, particularly involving gas absorption towers, are increasingly relevant in optimising AD systems. In this experiment, H₂ bubble-induced mixing enhances substrate, CO₂ and microbe contact, driving conversion and enhancing methane generation efficiency [7]. However, poor H₂ dispersion can also limit microbial access, demonstrating that microbial activity is paramount in this experiment [22]. This aligns with this finding, where microbial activity and reaction rates are affected by self-heating due to microbial metabolism, reinforcing the importance of thermal modelling in kinetic prediction



(a)



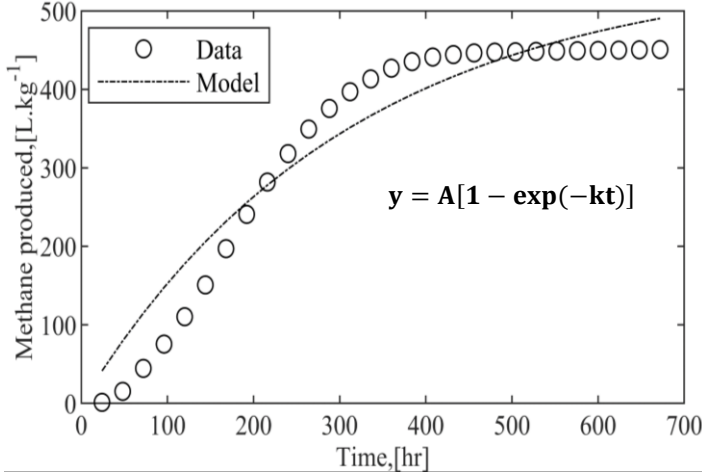
(b)

Figure 8 (a) and (b) shows CH₄ and CO₂ production without and with H₂ injection at a 0.69 ml/min rate

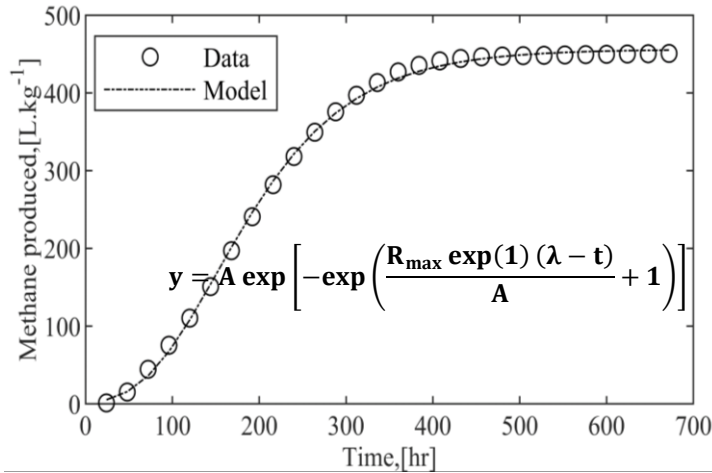
[20]. Integrating CFD techniques enables precise mapping of gas interactions, significantly enhancing the efficiency and accuracy of biogas systems [16]

4.5. Models

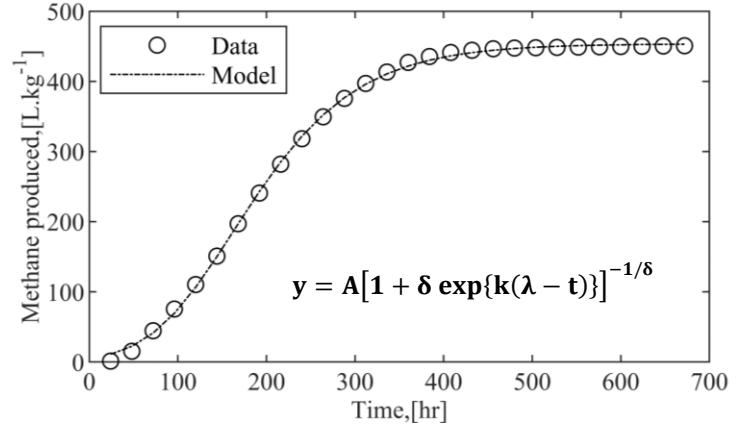
Figure 9 shows the kinetic model curve, where the First-order model was the least effective, achieving a coefficient of determination (R^2) of just 0.937. In contrast, the Modified Gompertz and Richards models boasted R^2 values exceeding 0.999, indicating that they align much more closely with the experimental data.



(a) First-Order Kinetic Model



(b) Modified Gompertz Model



(c) Richard Model

Figure 9. Comparison of Experimental Data with Predicted Biogas Production Models. (a) First-Order Kinetic Model (b) Modified Gompertz Model and (c) Richard Model. Each subplot illustrates the fit between experimental biogas production data (points and the corresponding model predictions (lines), highlighting their accuracy in describing the AD process.

Every model we examined included the lag phase, essentially the time it takes for microbes to adapt to their new environment, particularly at the beginning of anaerobic digestion[31]. Interestingly, the Richard and Modified Gompertz model was the most effective choice for simulating dynamic biogas systems. Energy analysis showed a net positive energy output, confirming that injecting H_2 in mesophilic environments is a promising approach [7]. The partial CH_4 enrichment we achieved aligns with the latest trends of upgrading biogas in the digester instead of doing it downstream.

Table 3. Developed models with their parameters and R^2 values.

Model	R^2 value	A (L.kg ⁻¹)	k (hr ⁻¹)	R_{max} (L.kg ⁻¹ .hr ⁻¹)	λ (hr)	δ
First-order kinetic	0.9367	553.74	0.0032	—	—	—
Modified Gompertz	0.9991	456.11	—	1.98	66.16	—
Richard	0.9994	453.53	0.0133	—	162.68	0.26

$$R^2 = 1 - \Sigma(y - \hat{y})^2 / \Sigma(y - \bar{y})^2 \quad \text{Equation (2)}$$

4.5.1 Model evaluation

The accuracy or evaluation metrics for the proposed kinetic models can be checked using R-squared (R^2), Equation (2). The R^2 value is between 0 and 1, with a higher value indicating a better model fit. Where y is the output, \bar{y} is the mean output of the data set, and \hat{y} is the

model output. A (L.kg^{-1}) is the biogas yield, k (hr^{-1}) is the first-order kinetic constant, R_{\max} ($\text{L.kg}^{-1} \cdot \text{hr}^{-1}$) is the maximal biogas production rate, λ (hr.) is the latency phase, and δ is the curve-fitting shape factor. These models were curve-fitted to the experimental data in MATLAB using the `lsqcurvefit` function.

These findings directly support local energy policy by demonstrating how a widely available, yet underutilised tropical crop waste derived from commonly consumed crops specific to Plateau State, Nigeria, can be transformed into renewable pipeline-quality methane. The decentralisation of H_2 enhanced AD for community-scale uptake is the sure way. Providing clean energy while reducing over-reliance on fossil fuels, informing policymakers, and empowering local farmers/entrepreneurs about its unique potential and viability. The energy will be integrated into the energy portfolio, fostering sustainable agriculture practices and promoting economic development.

5. Conclusion

This study presents novel mass transfer principles designed to purify biogas from distinct Plateau State, Nigeria feedstocks. It integrates kinetic models with energy optimisation methodologies to develop cost-effective and scalable anaerobic digestion systems compatible with Nigeria's energy framework.

This innovative approach significantly advances AD, aiming for biogas compositions comparable to pipeline-quality natural gas. Due to optimised fluid dynamics showed a 101.8% increase in biogas yield and a 110% increase in biomethane yield, alongside a 31.2% reduction in purity. The Richard Model ($R^2 = 0.99$) validated system performance, highlighting scalability for Nigeria's decentralised energy needs.

Despite incomplete CO_2 transformation due to mass transfer bottlenecks and microbial adaptation, the study highlighted the intricacies of in-situ biogas upgrading engineering. It created awareness of the need to concretise all parameterisations of process dynamics and microbial population management to ensure overall process stability.

While this study demonstrates the potential of in-situ H_2 injection to enhance CH_4 yield from tropical crop waste, certain limitations are acknowledged. First, lab-scale conditions (e.g., controlled mesophilic temperature, homogeneous feedstock) may not fully replicate real-world variability in decentralised systems. Second, the bioprocess kinetic modelling, though robust, assumes ideal microbial consortia behaviour without long-term

adaptation effects. Finally, economic and logistical scalability, such as H_2 sourcing in rural Nigeria or digester maintenance, requires further pilot-scale validation. These gaps present opportunities for future work in field trials and techno-economic analysis. Based on the findings, we recommend:

1. *Subsidies and training programs for local farmers (with small-scale digesters) using tropical crop waste, aligned with Nigeria's National Renewable Energy Action Plan.*
2. *Suggest collaboration and engagement with local government and community organisations to pilot biogas projects based on findings, reducing waste and supplementing LPG use*
3. *This initiative will reduce overreliance on dirty fuels (cow dung, charcoal, and firewood), open up capabilities for rural areas, and, in the long run, generate employment. It will also invariably address energy poverty, waste management, and climate objectives in Nigeria's pursuit of carbon neutrality by 2060.*

Future work should focus on continuous-flow systems, dynamic mixing strategies, and advanced microbial consortia to achieve higher methane purities and sustainable implementation at scale to achieve >90% CH_4 purities. This experiment is not a formality because it bridges theory and application, offering a practical path for Global South energy solutions.

Acknowledgements

The authors would like to thank Brunel University for the empirical work and the journal paper, LEAP Micro AD, for granting access to their Anaerobic Digester, particularly Rokia Yaman, for her technical expertise and support during the preliminary stages of the research. Celignis Limited and NRM part of Cawood for helping with the experiment. Also, Mrs Mercy Glong Emmanuel is acknowledged for providing the Finger Millet seed and waste used in the experiment. Lastly, I want to thank all the others who helped make the publication successful.

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