



# Article Examining the Potential of Biogas: A Pathway from Post-Fermented Waste into Energy in a Wastewater Treatment Plant

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Abstract: Biogas has improved due to technological advancements, environmental awareness, policy support, and research innovation, making it a more cost-effective and environmentally friendly renewable energy source. The Generalized Linear Model (GLM) was employed to examine the relationship between purchased and generated energy from 2007 to 2023. Metrics such as deviance, log likelihood, and dispersion phi were examined to assess model fit. The Mann–Kendall test was utilized to detect trends in energy datasets. Biochemical Oxygen Demand (BOD5) and Chemical Oxygen Demand (COD) reduction was significant, exceeding 97% from 2014 to 2023. However, treated sewage displayed limited susceptibility to biological degradation, with COD to BOD5 ratios increasing from 2.28 to 6.59 for raw sewage and from 2.33 to 7.05 for treated sewage by 2023. Additionally, the efficiency of sewage purification processes was calculated, and multivariate regression analysis was conducted on gas composition data. Principal Coordinate Ordination (PCO) and k-means clustering were used for dimensionality reduction and biogas component clustering, respectively. This research showed that biogas from the waste water treatment process can be used, particularly in methane production. Technological advancements have made biogas production more efficient, enhancing energy generation within a circular economy framework.

Keywords: biogas; circular economy; electricity production; heat assessment; sewage treatment

# 1. Introduction

Modern wastewater treatment plants are crucial components of infrastructure, purifying water of contaminants before it is reused or released into the environment [1]. Recently, artificial intelligence modeling has also been incorporated [2]. Biomethanation



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**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). occurs within anaerobic reactors, where living organisms decompose organic substances in the absence of oxygen [3-5]. This natural process results in the emission of methane and carbon dioxide, which are then extracted from the residual waste [6,7]. In wastewater treatment facilities, biomethanation offers significant advantages due to the substantial organic content present in wastewater, ideal for biogas production [8,9]. Throughout the wastewater treatment process, biogas is generated by treating sewage sludge, a byproduct of water purification [10]. Stored in anaerobic reactors, this sludge undergoes decomposition by microorganisms, yielding biogas. Subsequently, the biogas is purified to yield high-quality biomethane [11]. One of the significant challenges associated with biomethanation is the efficient utilization of the produced gas [12]. Methane is a highly valuable gas, but it requires an appropriate distribution and storage system. For biomethane, which is produced in smaller quantities than natural gas, it is essential to ensure suitable conditions for its distribution and storage to enable its effective use [13]. Biomethanation has many advantages. Firstly, it is an environmentally friendly process that reduces the amount of organic waste, such as food scraps and agricultural residues. Secondly, biomethane can be used as a green energy source, contributing to the reduction in greenhouse gas emissions. Thirdly, the biomethanation process can help develop new energy sources in rural areas [14]. The biomethanation process consists of two stages: hydrolysis and fermentation [15]. Hydrolysis is the process by which large organic molecules are broken down into smaller compounds such as sugars, organic acids, amino acids, and glycerol. This process is catalyzed by enzymes present in microorganisms. Fermentation is the second stage of biomethanation, during which sugars, organic acids, and amino acids are converted into a gas composed of methane and carbon dioxide. Methane is produced through the reaction between microorganisms and carbon dioxide. The entire process takes place in special biogas reactors [16,17]. Anaerobic co-digestion (AcoD) can utilize the spare fermentation capacity in existing wastewater treatment plants (WWTP) to produce excess biogas beyond the internal energy needs of the treatment plant. It is expected that, through the combination of AcoD and biogas upgrading, more wastewater treatment plants will become net energy producers [18]. Biomethanation also helps reduce greenhouse gas emissions because biogas is produced in a sustainable and renewable manner, contributing to the reduction in fossil fuel consumption [19].

In wastewater treatment plants, biomethanation allows for the use of sewage sludge to produce biogas, enabling the generation of both electrical and thermal energy and reducing the amount of waste produced by the treatment plants [20]. In studies, process water (PW) was treated using coagulation, and the generated sludge after treatment (GSAT) was converted into methane-rich gas. Coagulation and anaerobic digestion were combined to effectively sanitize PW and convert the by-products of coagulation into biogas. Wastewater treatment plants are key facilities in cities that ensure water reaches the required quality before being returned to the environment. Their energy consumption is the most critical cost of their operation, although the sludge produced in the treatment process can be subjected to anaerobic digestion to produce biogas [21–24]. This biogas is typically burned in a cogeneration reciprocating engine, which generates electricity fed into the grid and the heat necessary to maintain the required temperature in the digester. This energy recovery technique also prevents direct methane emissions from biogas into the atmosphere [25]. The growing demand for water and energy has highlighted the importance of energy-efficient anaerobic wastewater treatment; however, anaerobic effluents still contain a significant portion of total CH<sub>4</sub> production and are discharged into the environment without being utilized as a valuable energy source. The importance of long-term assessments of biogas production's environmental impacts, including greenhouse gas emissions, is crucial for improving biogas production and wastewater treatment [26]. Studies should explore a wider variety of organic substrates, including urban organic waste [27] and industrial byproducts, to enhance methane yield and optimize resource use [28]. Future research should also utilize sewage sludge or manage wastewater treatment for biogas production [29].

Research on energy production efficiency from wastewater treatment processes remains limited despite widespread biogas production reports from agricultural sources. This study aimed to achieve four objectives: (i) establishing a correlation between biogas composition and its calorific value; (ii) assessing efficiency indicators of the wastewater treatment process, focusing on Biochemical Oxygen Demand (BOD5) and Chemical Oxygen Demand (COD); (iii) evaluating the energy production potential derived from biogas postwastewater treatment, considering biogas components and their utilization; (iv) analyzing trends in potential energy generation following waste material fermentation.

#### 2. Materials and Methods

# 2.1. Characteristics of the Research Object

The wastewater treatment plant in Komorowice is located in the Silesian Voivodeship, Poland. In addition to the inflow of wastewater, the system includes a receiving station with wastewater storage tanks. There is also an inflow from stormwater overflow on the left bank of the Biała River at kilometer 9 + 760 along its course. The wastewater treatment plant is a technologically advanced facility divided into two main sections: wastewater treatment and sludge treatment. It operates as a mechanical–biological treatment facility utilizing anaerobic sludge processing, primarily based on the activated sludge method.

At the wastewater treatment plant, sludge undergoes a fermentation process that produces biogas, which is then used as fuel in cogeneration units to generate both electricity and heat. The maximum wastewater discharge capacity of the plant is 1.44 m<sup>3</sup>/s, with an average daily discharge of 124,800 m<sup>3</sup>. Additionally, the local company manages a sewage network exceeding 1290 km across the municipality, operating 43 sewage pumping stations. Combined, these facilities have a total treatment capacity of 138,000 m<sup>3</sup> per day and process an annual volume of approximately 32.85 million m<sup>3</sup> of wastewater.

The treatment plant is equipped with two mechanical belt thickeners and two gravity thickeners, which are used to concentrate excess sludge before directing it to the fermentation chambers. The sludge from the gravity thickeners is combined with the sludge received from the waste reception station and the sludge thickened by the belt thickeners before being sent for fermentation. The introduction of sludge to the thickeners is carried out using sludge feed pumps, while the transfer of thickened sludge to the fermentation chambers is performed using thickened sludge pumps. Mechanical thickening of the sludge requires the addition of a polyelectrolyte, which is prepared at the polyelectrolyte station and added via polymer pumps. After mixing with the polyelectrolyte, the excess sludge is introduced onto the filter belt. The thickening process using thickeners occurs through gravitational means.

# 2.2. Description of the Technological Process at the Wastewater Treatment Plant

The type of waste introduced into the biogas production process was municipal waste. The substrate for fermentation primarily consists of thickened excess activated sludge. Additionally, waste brought to the processing station is also included in the fermentation process. The daily amount does not exceed 100 t/d, which can account for a maximum of up to several percent of the volume of the excess sludge stream. Raw sewage passes through a gravel trap, then it proceeds to screens and sand washers to capture larger impurities, including debris. In the subsequent stage of the process, mineral pollutants are removed through sedimentation in the sand trap. In the next step, there is the process of pumping the preliminarily treated sewage and sludge. Later, there is a gravitational sludge thickener, where excess sludge is thickened for fermentation chambers. The effluent in the co-fermentation process consisted of pre-dewatered sewage sludge and grass clippings from mowing residential gardens. The bioreactor is utilized for purification in biological processes, where sewage aeration occurs. Additionally, to reduce nitrate nitrogen, in each of the final nitrification chambers, a sediment transfer system to the denitrification zone is installed—internal recirculation is performed by pumping mixers (a total of 3 pieces), dependent on the concentration of nitrate nitrogen in the denitrification zones. After the

aeration process, the sewage is directed to the coagulant dosing station, where the addition of PIX is conditioned by the analysis of phosphates at the outlet after the secondary settler. The final clarification of sewage occurs in a secondary settling tank equipped with sludge scraping devices. Excess sludge, in turn, is recirculated. During periods of intense rainfall, the stormwater settler also operates. The technological line also includes a retention tank for delivered sewage and emergency tanks storing excess sewage during periods of heavy rainfall. The general plan of the technological procedure is depicted in Figure 1.



Figure 1. A technological procedure in the wastewater treatment plant.

The Komorowice Wastewater Treatment Plant uses the activated sludge method for treatment. Sludge is fermented to produce biogas, which is then directed to a storage tank through a desulfurization unit that utilizes activated carbon. The carbon is replaced when the hydrogen sulfide levels in the exiting biogas exceed acceptable limits. Additionally, devices for removing silicon compounds from the biogas are installed. The biogas storage tank is a membrane tank with a capacity of 2100 m<sup>3</sup>, designed in the shape of a truncated

sphere using UV-resistant PVC-coated polyester. The operating pressure in the tank is maintained at 15 mbar (1.5 kPa) by creating a slight overpressure in the space between the outer and inner membranes. The biogas installation includes connection chambers with automatic drainage systems. A biogas flare with a capacity of  $350 \text{ Nm}^3/\text{h}$  features a concealed combustion flame and is designed to burn off excess biogas produced or to handle failures in the cogeneration units. The flare activates automatically when the tank reaches 95% capacity, leading to the automatic supply and ignition of biogas, and extinguishes when the tank capacity drops to 90%. The biogas collected in the gas tank is fed into the cogeneration unit building, which houses units with electric powers of 450 kW and 365 kW. Biogas is burned in cogeneration units to generate electrical energy for the external grid and thermal energy for heating sludge treatment devices, meeting approximately 40% of the wastewater treatment plant's energy needs. Additionally, biogas is used to produce self-generated electricity that powers the technological equipment of the plant and provides thermal energy needed to heat the fermentation chambers and warm the sewage sludge within them. The heat source consists of waste heat generated by the two cogeneration units and a local boiler house equipped with two biogas-fired boilers. When biogas supply is insufficient, the boilers can also utilize natural gas as an alternative fuel for heating.

## 2.3. Statistical Analysis of Research Results

We explored the relationship between purchased energy and generated energy using the Generalized Linear Model (GLM), which offers a more advanced way to analyze this connection compared to simpler linear models. By selecting the identity function within the GLM, we could appropriately model the data, considering its distribution from 2007 to 2023. In our analysis, the intercept (b) played a crucial role, indicating the level of generated energy when purchased energy is at zero. Its high value (3,218,400) suggests there are fixed costs or a minimum level of activity required for energy generation. To assess how well our model fits the data, we examined metrics like deviance and log likelihood. Lower deviance values suggest a better fit, while higher log likelihood values indicate a stronger match. Additionally, we considered dispersion phi, which measures how spread out the data points are around the regression line, with higher values indicating greater dispersion. The G statistic and p(slope = 0) are crucial for gauging the statistical significance of the slope coefficient. A higher G statistic reflects a more significant deviation of the slope coefficient from zero, while a lower p(slope = 0) value indicates increased statistical significance.

Moving to trend analysis, the Mann–Kendall test serves as a valuable non-parametric tool for detecting trends in temporally or spatially ordered data. In our study, we applied this test to both generated and purchased energy datasets. A larger S value signifies a stronger trend, while the Z statistic measures the deviation from the expected value in the absence of a trend.

Based on the physicochemical indicators of raw and treated sewage from the years 2014–2023, the efficiency of the purification process was calculated using the results of the biological breakdown of organic matter. Additionally, the ratios of COD/BOD5, COD/TN, COD/TP, BOD5/TN, and BOD5/TP were calculated. Multivariate regression analysis was conducted, with the calorific value as the dependent variable and the gas composition, including carbon dioxide, hydrogen sulfide, methane, and oxygen, as the independent variables. Principal Coordinate Ordination (PCO), also known as Multidimensional Scaling (MDS), is a dimensionality reduction technique similar to Principal Component Analysis (PCA) but primarily used for distance or non-Euclidean data. PCO is employed when data are in the form of a distance matrix between observations, aiming to reduce the dimensionality of data while minimizing the loss of information about distances between observations. The data collected for biogas composition included methane, carbon dioxide, oxygen, and hydrogen sulfide, along with the heating value. To analyze these data, the k-means method was used for clustering. In this context, WGSS (Within-Group Sum of Squares) calculates the sum of squared distances within each cluster. Essentially, it gauges

how similar the objects within a cluster are to each other. It is computed by summing up the squared distances between each data point and the centroid of its cluster. A lower WGSS value indicates tighter, more homogeneous clusters, reflecting how compact they are. Minimizing WGSS is a common objective in the optimization process of k-means clustering, aiming to achieve more cohesive groupings of data points. The analysis was performed using the PAST 4.17 software. Moreover, a box-whisker plot was created in Excel 2019 for the dominant components produced in the biogas production process.

# 3. Results

## 3.1. Parameters of Raw and Treated Sewage

The analysis presented focuses on the operation of the wastewater treatment plant over the years 2014–2023. During this period, the highest average BOD5 value was  $303 \text{ mg} \cdot \text{dm}^3$ , and COD was at 722 mg  $\cdot \text{dm}^3$  in the year 2022. It was similar for TSS and total nitrogen. Meanwhile, for total phosphorus, the maximum average annual value reached 5.9 mg  $\cdot \text{dm}^3$  in the years 2018 and 2021 (Table 1).

Year	BOD5	COD	TSS	NT	РТ
			(mg·dm <sup>−3</sup> )		
2014	259	590	316	43	6.58
2015	289	584	324	43.2	6.19
2016	220	487	240	39	5
2017	231	503	265	41.2	4.98
2018	266	597	287	47.4	5.9
2019	241	564	299	42.7	5.42
2020	236	535	295	41.4	4.96
2021	259	575	302	43.6	5.9
2022	303	722	373	48	5.49
2023	250	583	342	41.2	5.37

**Table 1.** The average annual physicochemical parameters in raw sewage.

Considering the same research period, the highest average annual value of BOD5 in treated sewage was 6.6 mg·dm<sup>-3</sup>, while COD was at 46.5 mg·dm<sup>-3</sup> in the year 2023. Similarly, for TSS, the maximum average annual value was 11.4 mg·dm<sup>-3</sup> in the first year of the study (2014). For total nitrogen, a value of 8.78 mg·dm<sup>-3</sup> was recorded twice in the years 2015 and 2023. Meanwhile, for total phosphorus, the highest average annual value reached 0.6 mg·dm<sup>-3</sup> in the year 2016 (Table 2).

Table 2. The average annual physicochemical parameters in treated sewage.

Year	BOD5	COD	TSS	NT *	РТ	
			(mg·dm <sup>−3</sup> )			
 2014	5.89	38.8	11.4	8.21	0.48	
2015	5.2	34.6	10.4	8.78	0.45	
2016	5.52	39	11	8.7	0.6	
2017	5.4	35.4	9	8.56	0.41	
2018	5.85	41.4	9.3	8.21	0.4	
2019	5.68	39	8.4	8.14	0.43	
2020	5.91	38.9	8.9	8.03	0.46	
2021	5.71	38.6	8.4	8.36	0.48	
2022	5.92	40.9	8.9	8.18	0.44	
2023	6.6	46.5	11	8.78	0.5	

\* for temperatures in the bioreactor >12 degrees Celsius.

The highest value of the average annual sewage inflow reached 21.550867 million  $m^3$  in 2020. Meanwhile, the maximum quantity of sewage delivered to the purification process was 105.000  $m^3$ ·year<sup>-1</sup> in the last year of the study (Table 3).

Year	The Amount of Sewage Flowing from the Sewer System	The Amount of Sewage Delivered from Vacuum Trucks		
	Million $m^3 \cdot year^{-1}$	m <sup>3</sup> ·year <sup>−1</sup>		
2014	20.951997	98,000		
2015	18.846241	54,000		
2016	20.042773	40,000		
2017	20.553211	30,000		
2018	18.390084	32,000		
2019	20.166631	38,000		
2020	21.550867	53,000		
2021	20.862850	63,000		
2022	18.946610	64,000		
2023	21.315280	105,000		

**Table 3.** The average annual amount of sewage flowing into the wastewater treatment plant used in the research.

In most cases, the reduction in BOD5 and COD was significant. For example, in 2014, it was over 97%, similar to 2023. However, treated sewage showed poor susceptibility to biological degradation. For example, the COD to BOD5 ratio for raw sewage was 2.28, and for treated sewage, it was 6.59. In 2023, the ratio for raw sewage was 2.33, and for treated sewage, it was 7.05 (Table 4).

Table 4.	The susce	ptibility of	f raw and	treated	sewage to	the biolo	gical de	gradation	process.
							0	0	

COD/PT	COD/NT	BOD5/PT	BOD5/NT	COD/BOD5	Sewage Type	Year
89.67	13.72	39.36	6.02	2.28	raw	2014
80.83	4.73	12.27	0.72	6.59	treated	
94.35	13.52	46.69	6.69	2.02	raw	2015
76.89	3.94	11.56	0.59	6.65	treated	
97.40	12.49	44.0	5.64	2.21	raw	2016
65.0	4.48	9.2	0.63	7.07	treated	
101.00	12.21	46.39	5.61	2.18	raw	2017
86.34	4.14	13.17	0.63	6.56	treated	
101.19	12.59	45.08	5.61	2.24	raw	2018
103.50	5.04	14.63	0.71	7.08	treated	
104.06	13.21	44.46	5.64	2.34	raw	2019
90.70	4.79	13.21	0.70	6.87	treated	
107.86	12.92	47.58	5.70	2.27	raw	2020
84.57	4.84	12.85	0.74	6.58	treated	
97.46	13.19	43.90	5.94	2.22	raw	2021
80.42	4.62	11.90	0.68	6.76	treated	
131.51	15.04	55.19	6.31	2.38	raw	2022
92.95	5.00	13.45	0.72	6.91	treated	
108.57	14.15	46.55	6.07	2.33	raw	2023
93.0	5.30	13.20	0.75	7.05	treated	
>40	$5\div 10$	>20 (optimum 25)	>2.5 (optimum 4)	<2	The required valu wastewater t	le for effective reatment

The trend analysis showed a good fit for the fermentation process of utilized waste, with an  $R^2$  value of 0.68. Analyzing the amount of waste from wastewater treatment plants directed to fermentation, a significant increase is evident, particularly during the years 2020–2023 (Figure 2).



Figure 2. Amount of waste for fermentation during the study period.

# 3.2. Energy Analysis from Biogas Production

Analyzing the figure, it is clear that more energy was purchased than was generated. Since 2011, there has been an increase in generated energy from 200,000 to 400,000 annually (Figure 3). Generally, methane dominated the composition of the resulting biogas (with a median of 61.6%). Carbon dioxide was the second most abundant component with a median of 37.7% (Figure 4). Additionally, hydrogen sulfide was detected in the biogas, with a median concentration of 50 ppm, and the oxygen content was less than one percent. In the examined composition of produced biogas. the calorific value systematically increased with the rise in methane levels. A linear trend was observed with an R<sup>2</sup> value of 0.92 (Figure 5). However, no such correlation was noted for CO<sub>2</sub> concentrations.







Figure 4. Main components of the biogas produced in the technological process (n = 203).



Figure 5. Relationship between calorific value and methane content.

Analysis of electricity consumption and production data spanning from 2007 to 2023 unveils notable trends. Both purchased and generated electricity experienced consistent growth over the years. Notably, the proportion of self-generated energy within total consumption surged from 18% in 2007 to 41% in 2023. The arithmetic mean of this self-generated energy share stood at approximately 31.52%, with a standard deviation indicating variations of around 7.23% around this mean. The median of the share of self-generated energy was slightly higher, at around 32.78%. The variance is relatively low, indicating stability in the shares of self-generated energy over the analyzed period. Skewness for purchased energy is minimal, but for generated energy, it is negative, suggesting asymmetry in the data. Since 2007, there have been upward trends in self-generated energy production, indicating potential economic or ecological benefits. Additionally, the increasing share of self-generated energy in overall consumption suggests a greater utilization of renewable energy sources or more efficient energy systems. During the initial period of the study,



waste deliveries for co-fermentation did not exceed 5,000 tons. A significant increase in waste deliveries has only been noticeable since 2020 (Figure 6)

Figure 6. Amount of waste received for co-fermentation in the years 2014–2023 with a 5-year forecast.

The results of Mann–Kendall test for purchased energy (S = 30, Z = 1.30, p = 0.19) suggested that there is no statistically significant trend. The probability of a trend is relatively high (0.19167), indicating a lack of convincing evidence for a trend in the purchased energy data. The results of Mann–Kendall test for generated energy (S = 60, Z = 2.65, p = 0.0078) indicated the presence of a statistically significant increasing trend. The *p*-value is significantly lower compared to purchased energy, suggesting convincing statistical evidence for an increasing trend in the generated energy data.

PCO, similar to PCA, considers linear correlations between variables, but its focus is on distances between observations rather than variable variance. In the PCO results, 93.99% of variance was observed for the first coordinate axis. with 5.98% for the second (Figure 7).

Our results in the context of k-means clustering showed that an F-statistic of 1.58 suggested the clusters were relatively similar to each other, with higher F values typically indicating better-separated clusters. The variance of 61.314 pointed to a high level of variability in the data. The average silhouette score of 0.56 indicated that the clusters were moderately well separated, as this metric measured how well objects fit within their clusters, with values ranging from -1 to 1. A score of 0.56 suggested moderately good clustering quality, where values close to 1 denoted well-separated clusters, values near 0 indicated overlapping clusters, and values below 0 implied misclassified objects. Lastly, the WGSS (Within-Group Sum of Squares) value of 2.311 indicated that the clusters were relatively compact and homogeneous (Figure 8).

The positive slope of 0.012 with a small standard error suggests that methane has a significant positive effect on the dependent variable. The high correlation coefficient (r = 0.96) indicates a strong positive linear relationship between methane and the dependent variable—the calorific value. The negative slope of -0.0041 with a relatively large standard error suggests that carbon dioxide has a significant negative effect on the dependent variable. The correlation coefficient (r = -0.26) indicated a moderate negative linear relationship. The slope and error are both zero. indicating that there is no relationship between oxygen and the dependent variable. The positive slope of 0.080 with a moderate standard error suggests that hydrogen sulfide has a significant positive effect on the dependent variable. The correlation coefficient (r = 0.30) indicated a moderate positive linear relationship (Table 5).



**Figure 7.** PCO for biogas composition: red diamonds represent heating value, blue squares denote methane, black squares stand for hydrogen sulfide, and green stars symbolize oxygen.



Figure 8. K-means analysis for clustering biogas components.

р	r	Error	Intercept	Error	Slope	Variable
>0.001	0.96	1.18	2.40	0.0002	0.012	Methane
0.00011	-0.26	5.14	57.98	0.0010	-0.0041	Carbon dioxide
>0.001	0.30	87.57	-338.56	0.017	0.080	Hydrogen sulfide

Table 5. Multivariate linear regression for the main biogas components.

# 4. Discussion

# 4.1. Biogas and the Circular Economy

The imperative of the circular economy is increasingly evident in waste management and biogas utilization. In our investigation, a substantial volume of waste underwent fermentation, notably including an escalation in wastewater treatment waste by 2000 Mg annually, as indicated by an  $R^2$  of 0.68 (Figure 2). Addressing energy management emerges as paramount, urging the exploration of techniques fostering enhanced energy efficiency. While our analyses revealed no statistically significant Mann–Kendall trend for purchased energy, a noteworthy upward trend was evident for generated energy, reaching 4,000,000 kWh·year<sup>-1</sup> in the final year of observation (Figure 3). Importantly, findings underscored that greenhouse gas emissions across the entire value chain are lower for biogas compared to alternative fuel options. Leveraging energy from solid municipal waste and sewage, our study suggests a potential displacement of 4053.47 t of diesel fuel daily, showcasing promising avenues for sustainable energy solutions.

Heat demand for a 50,000-resident plant in Spain: 28–51%, EUR 38–65/MWh [30]. MSP of biomethane: GBP 135–183/MWh, potential reduction: 32–42% [23]. Additionally, the produced gas demonstrated versatility, capable of powering a 50 kW generator for 5.5 to 9 h with specific feedstock mixtures [31]. However, critical levels of H<sub>2</sub>S and HCl were noted in the biogas, with concentrations reaching 1570 and 26.8 mg  $\cdot$ m<sup>-3</sup>, respectively, while levels of halogenated VOCs and mercaptans were relatively low [32]. WWTPs distant from high-pressure networks can produce renewable biomethane to replace local natural gas. Economic viability is uncertain; selling CO2 at EUR 46 per t is needed for profitability, while feed-in premiums over EUR 55.5 per MWh may also be required [32]. Understanding the complexity of dependent variables, such as generated energy (Y), is paramount. Its determination can be influenced by various factors including purchased energy, weather conditions, and seasonal trends. Within our Generalized Linear Model (GLM), we focused on the influence of purchased energy on generated energy. The model's findings unveiled a negative slope coefficient (-0.10852), indicating a negative relationship between purchased energy and generated energy. In simpler terms, as purchased energy increases, generated energy decreases. While the Mann-Kendall test results for purchased energy revealed no statistically significant trend (S = 30; Z = 1.30; p = 0.19), suggesting insufficient evidence for a trend, generated energy exhibited a notable increasing trend (S = 60; Z = 2.65; p = 0.0078), supported by robust statistical evidence with a lower *p*-value. This underscores the upward trajectory in generated energy data.

## 4.2. Biogas Production Potential from Agricultural and Industrial Organic Waste

Now, agricultural sources are being utilized for biogas production, with a focus on comparing the renewable energy potential of food and beverage industry waste, evaluating development barriers, and emphasizing the increasing use of industrial organic waste in biogas production as a cost-effective alternative to maize silage [33]. In the other studies, substrates were subjected to anaerobic fermentation, and biogas production was measured. Food waste substrates exhibited higher methane yield ranging from 354 to 347 mL·g-TCOD<sup>-1</sup> and biodegradability of 89 ÷ 87%. For sludge substrates, the yield was from 324 to 288 mL·g-TCOD<sup>-1</sup> with biodegradability of 81–73%. It was also estimated that coffee waste has the potential to generate energy recovery between 4 and 10 million kJ·day<sup>-1</sup> and organic fertilizer (digestate) at the level of 18.8–25.2 kg·day<sup>-1</sup> [34]. Energy balance studies demonstrated the possibility of combining remediation with energy production.

The high photosynthesis rate and ability to generate biomass along with nutrient uptake advocate for the use of microalgae as a potential source of next-generation biofuel in waste management [35].

Five main waste streams were identified as potential substrates for biogas production, namely slaughterhouse waste (consisting of dewatered activated sludge); wastewater from cheese factories; commercial and domestic food waste; pig slurry; and sewage sludge. The biomethane potential from these waste streams ranged from as low as 99  $CH_4 \cdot kg^{-1}$  for pig slurry to as high as 787  $CH_4 \cdot kg^{-1}$  for cheese factory wastewater sludge using dissolved air flotation (DAF) [36]. A series of batch experiments were conducted to determine the biomethane potential from three different sewage sludge samples over 74 days, using zinc content in the sludge, either alone or in combination with external addition of 200, 300, and 400 mg Zn/L. In the analysis of Principal Component Ordination (PCO), the data revealed that the first coordinate axis accounted for 93.99% of the variance, indicating its significant influence on the data structure, while the second axis explained 5.98%, representing a lesser degree of variation. Notably, hydrogen sulfide distribution across axes, barring one quadrant in the third axis, suggested either minimal differentiation from other variables or specific relationships with them. This underscores the strong association of data with the first coordinate axis, signifying a predominant variable influencing the data structure. Meanwhile, methane and heating value components exhibited a strong correlation, contrasting with the occasional negative correlations observed with carbon dioxide (Figure 7). The highest biomethane production was  $165 \pm 1 \text{ mL CH}_4/\text{g}$  with the use of activated sludge (AS) with a background concentration of 93 mg Zn/L. A slight decrease in biomethane yield (i.e.,  $157 \pm 1.158 \pm 1$ . and  $159 \pm 1 \text{ mL CH}_4 \cdot \text{g}^{-1}$ ) was obtained in the presence of 293, 393, and 493 mg Zn/L, respectively [15]. Anaerobic digestion (AD) is a biological process that naturally occurs when bacteria break down organic matter in an environment with or without oxygen. Almost any organic material can be processed in AD, including paper and cardboard (too low-grade for recycling due to food contamination), grass clippings, food scraps, industrial wastewater, and animal waste, AD produces biogas, which consists of approximately 60% methane and 40% carbon dioxide [37]. Our study identified four main gases, with methane comprising approximately 60% and carbon dioxide around 40% of the composition from 2014 to 2023 (Figure 4). Methane exhibited a robust correlation ( $R^2 = 0.92$ ) with the calorific value of the resulting biogas, affirming its status as the primary component essential for achieving a calorific value above 20 MJ·m<sup>-3</sup> (Figure 5).

Currently, there is a growing interest in analytical methodologies for sampling and analyzing biogas from various wastewater treatment plants across Europe, as noted by [37]. Additionally, emerging trends include the transformation and utilization of biogas from diverse sources within the framework of the Green Energy Transformation, as highlighted by [38]. In our study, a large amount of waste was subjected to the co-fermentation process. There is a strong upward trend in the influx of supplied waste, exceeding 5000 Mg annually with an  $R^2 = 0.99$  (Figure 6). This indicates a constantly growing need for technological changes, as the waste can include a variety of biological substances [39,40]. This proportion is highly favorable from the perspective of our research findings. A higher methane content relative to  $CO_2$  can significantly enhance the calorific value of the produced biogas. In our paper, it was shown that the level of  $CO_2$  in the biogas production process does not significantly affect the calorific value. The highest content was observed for methane with  $R^2 = 0.92$  (Figure 4), which suggests that treatment plants should focus more on monitoring methane levels rather than carbon dioxide and hydrogen sulfide levels.

Regarding k-means clustering, the results depicted moderate effectiveness, with a Within-Group Sum of Squares (WGSS) value of 2.311 representing relatively compact and homogeneous clusters. The F-statistic of 1.58 implied similarities between clusters, while the variance of 61.314 indicated substantial variability within the dataset. Moreover, an average silhouette score of 0.56 suggested moderately well-separated clusters. While these metrics showed reasonable effectiveness, there exists potential for optimization, possibly

through adjustments in cluster numbers or alternative clustering algorithms. The study also emphasized the significance of methane and carbon dioxide in biogas analysis, evident from their distinct clustering (Figure 8).

In multivariate regression analysis spanning from 2014 to 2023, a clear relationship between the technological process and variables was revealed, particularly their impact on calorific value. Methane exhibited a significant positive effect, while carbon dioxide had a notable negative impact. Conversely, oxygen showed no discernible relationship, and hydrogen sulfide displayed a significant positive effect on calorific value. These insights underscored a comprehensive understanding of the intricate relationships within the technological framework of biogas production. This comprehensive analysis offers valuable insights into the dynamics of biogas production, highlighting methane's crucial role, the importance of managing carbon dioxide levels, and the intriguing dynamics of oxygen and hydrogen sulfide. These findings provide a basis for optimizing production processes, enhancing energy efficiency, and minimizing environmental impact, necessitating further research to deepen our understanding for a sustainable energy future and waste management.

## 4.3. Key Indicators of Limitations in Nutrient Removal Efficiency of Wastewater Treatment

Several key indicators highlight the limitations in wastewater treatment efficiency, particularly concerning nutrients, Chemical Oxygen Demand, and Biochemical Oxygen Demand. First, the balance between BOD5 and nitrogen is critical; low BOD5 to N ratios can inhibit the growth of denitrifying microorganisms, which reduces nitrogen removal efficiency and may lead to elevated nitrate levels in the effluent.

In raw wastewater, the BOD5 values ranged from 220 to 303 mg·dm<sup>-3</sup>, while COD values ranged from 487 to 722 mg·dm<sup>-3</sup> during the study period. TSS reached a maximum value of 373 mg·dm<sup>-3</sup> in 2022, and NT reached 47.4 mg·dm<sup>-3</sup> in 2019. On the other hand, PT reached its maximum value in 2014 (Table 1). In treated wastewater, the BOD5 range was from 5.4 to 6.6 mg·dm<sup>-3</sup>, and COD values ranged from 34.6 to 46.5 mg·dm<sup>-3</sup>. The highest TSS was recorded in 2014, at 11.4 mg·dm<sup>-3</sup>. NP in treated wastewater was highest in 2015 and 2023, at 8.78 mg·dm<sup>-3</sup>, while PT did not exceed 1 mg·dm<sup>-3</sup> (Table 2). A low ratio of BOD5 to nitrogen (N) causes inhibition of the growth of denitrifying microorganisms. thereby reducing the efficiency of nitrogen compound removal. The biological degradation of pollutants is measured by the ratio of COD to BOD5 [26]. Typically, efficient degradation is observed when this ratio is less than 2. Higher values of the COD/BOD5 ratio reduce the effectiveness of the biological degradation process. The presence of substances resistant to biodegradation (COD/BOD5 >> 2) may result in inadequate denitrification [26].

Despite the high efficiency of wastewater treatment, the biodegradability of the treated wastewater was low. This indicates the presence of a large amount of non-degradable substances. For example, the COD/BOD5 ratio in raw wastewater was 2.28, while in treated wastewater it was 6.59 in the first year of the study. An unfavorable reference value for the BOD5/NT ratio was noted in treated wastewater. A favorable reference value was observed for raw wastewater, as it exceeded 20 dm<sup>3</sup>. In contrast, a favorable situation was observed in treated wastewater for all the years of the study. The COD/PT ratio in both raw and treated wastewater reached the required value for effective wastewater treatment (Table 4). These results indicate an uneven biological decomposition process and a high accumulation of hardly degradable compounds. The effectiveness of biological phosphorus removal can be assessed based on the ratio of easily degradable organic substances to phosphorus content, i.e., the ratio of BOD5 to phosphorus. It is generally accepted that this ratio should be at least 20, and for low-loaded wastewater, it should be equal to or greater than 25. An unfavorable ratio of BOD5 to nitrogen can hinder the denitrification process, resulting in partial denitrification consequently leading to an increase in nitrates at the outflow. Denitrification proceeds without disturbances when the ratio of COD to nitrogen ranges from 5 to 10. Low values disrupt the process and necessitate the dosing of an external source of organic carbon.

Industry wastewater was treated with a BOD ratio of 100 during the biological treatment of wastewater [41]. Ref. [42] showed that significantly lower COD/N ratios resulted in decreased biological removal efficiency. In low-strength wastewater, the COD/P ratio was found to be  $15:1 \div 25:1$  [26]. The values of the CODCr/BOD5 ratio for raw sewage ranged from 1.9 to 2.5. while for sewage after successive mechanical treatment processes they ranged from 1.8 to 2.8. For sewage after biological processes, the ratio varied between 1.8 and 4.9. The increase in the ratio during the technological treatment process is associated with the breakdown of organic compounds. High CODCr/BOD5 ratios for treated sewage (3.1–9.8) specify that they mainly contain biologically hard-to-degrade organic substances [43].

Based on the insights gleaned from these studies, it is advisable to not only progress agricultural biogas plants but also to delve into the development of biogas facilities utilizing sewage sludge from wastewater treatment plants [44]. In 2015, the European Union demonstrated significant strides in biogas development, boasting an impressive 18 billion m<sup>3</sup> in methane production, driven by renewable energy policies and resulting in substantial economic and environmental advantages. With over 10 GW of installed capacity and 17,400 biogas plants, the EU solidified its position as the global leader in biogas electricity generation, contributing to a sustainable energy landscape [45]. Contemporary approaches entail harnessing organic waste for the creation of biomentation processes [46–48]. To enhance wastewater treatment and biogas production, it is recommended to advance sewage biogas plants and develop facilities utilizing sewage sludge to optimize methane production through renewable energy policies [49,50].

# 5. Conclusions

This study revealed that methane exhibited the highest correlation with its calorific value. Assessing the efficiency indicators of the wastewater treatment process, particularly Biochemical Oxygen Demand (BOD5) and Chemical Oxygen Demand (COD), showed unfavorable ratios for COD/BOD in the treated effluent, despite highly efficient removal exceeding 90%. Although the BOD5/NT ratio in treated wastewater was unfavorable, it remained favorable in raw wastewater. However, the COD/PT ratio met the required value for effective wastewater treatment in both raw and treated wastewater. Evaluating the energy production potential derived from biogas post-wastewater treatment revealed a significant statistical trend of increased generated energy, considering biogas components and their utilization. Understanding the biodegradability of treated wastewater is crucial as it indicates the effectiveness of wastewater treatment processes and highlights areas for improvement in fermentation bioreactions. This knowledge drives innovation by using confirmation methods that are new in wastewater management practices, supporting environmental sustainability. Analyzing trends in energy generation from waste fermentation, we found that methane and carbon dioxide were the key predictors for biogas components. This study introduces new findings on k-means clustering, showing moderate effectiveness with a WGSS of 2.311 and an F-statistic of 1.58. The average silhouette score of 0.56 indicates moderately well-separated clusters, suggesting potential for optimization. The significance of methane and carbon dioxide in biogas analysis is highlighted through their distinct clustering. Such insights offer valuable advancements in understanding and optimizing biogas production processes for improved energy efficiency and environmental sustainability. This research introduces a new approach by analyzing the composition of the resulting biogas to assess specific relationships. This requires long-term research spanning at least 10 years, as this extended period is standard for data analysis. This duration allows for the evaluation of biogas production and purification effects for circular economy as they delineate the path from sludge to resource. This procedure entails directing the residues of waste materials to fermentation processes subsequent to their separation during the purification stage.

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