energies

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Fallen Leaves as a Substrate for Biogas Production

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Abstract: Fallen leaves in cities are often treated as waste; therefore, they are collected, transported outside urban areas, and composted, which contributes to greenhouse gas (GHG) emissions. Instead of this conventional management approach, fallen leaves could be utilized as a feedstock in biogas production, helping to reduce GHG emissions, increase renewable energy generation, and provide fertilizer. The aim of this study was to compare the mono-digestion of fallen leaves from three tree species commonly found in parks and along streets—northern red oak (*Quercus rubra* L.), small-leaved lime (*Tilia cordata* Mill.), and Norway maple (*Acer platanoides* L.)—in both wet and dry anaerobic digestion (AD) systems. A biochemical methane potential (BMP) test was conducted in batch assays for each of the three substrates in both AD technologies at a temperature of 38 ± 1 °C. The highest specific methane yield (SMY) was obtained from *Quercus* leaves in wet AD technology, with a methane yield of 115.69 ± 4.11 NL kg_{VS}^{-1}. The lowest SMY (55.23 ± 3.36 NL kg_{VS}^{-1}) was observed during the dry AD of *Tilia* leaves. The type of technology had no significant impact on the SMY of *Acer* and *Tilia* leaves; however, the methane yield from *Quercus* leaves in wet AD was significantly higher ($p < 0.05$) than that from dry AD. Studies on the use of fallen leaves from *Tilia cordata*, *Quercus rubra*, and *Acer platanoides* as substrates in mono-digestion technology have shown their limited suitability for biogas production. Nevertheless, this feedstock may be more effectively used as a co-substrate, mainly due to the low concentrations of ammonia (NH_3) and hydrogen sulfide (H_2S) in the biogas produced from these leaves, both of which are considered inhibitors of the AD process.

Keywords: wet anerobic digestion; dry anaerobic digestion; specific methane yield

Citation: Wysocka-Czubaszek, A.; Czubaszek, R. Fallen Leaves as a Substrate for Biogas Production. *Energies* **2024**, *17*, 6038. https://doi.org/10.3390/en17236038

Academic Editor: João Fernando Pereira Gomes

Received: 25 October 2024
Revised: 15 November 2024
Accepted: 29 November 2024
Published: 1 December 2024

1. Introduction

The growing concern about the quality of life in cities, where citizens feel the impact of global warming more and more regularly and severely, has resulted in developing and implementing urban adaptation strategies to climate change. These adaptation actions introduce nature-based solutions aimed at developing resilient cities. Such solutions include, among others, maintaining, restoring, and creating parks and urban forests, as well as planting individual urban trees [1]. The maintenance and management of urban trees involve managing their growth, as well as addressing issues such as fallen flowers, leaves or fruits. Since growing trees in urban spaces is one of the essential actions preventing the increasing temperature in cities together with purifying air, preserving ecosystems, and reducing stress [2], the waste generated during their maintenance is becoming a growing problem. The management of fallen leaves causes a significant workload, high transportation costs [3], and greenhouse gas (GHG) emissions. The sustainable management of fallen leaves requires environmentally friendly and economically justified solutions. In most urban areas, fallen leaves are raked and then composted. However, in several Polish cities, programs to reduce the amount of leaf-raking have been introduced. Leaving the leaves on the ground improves soil quality, retains and stores water, reduces evaporation from soil, protects organisms and plants from freezing, and provides shelter and food to many organisms [4]. However, the most representative places and those that are often used, as well as leaves from trees and shrubs that have been attacked by pests and diseases, have to be raked. Fallen leaves should also be collected in places where they can clog gutters or street drains and increase the risk of accidents caused by making roadways slippery. Therefore, the problem of fallen leaves still exists. Fallen leaf composting is one of the most common environmentally friendly management options, which, as a final product, offers a valuable soil amendment. However, two of the main challenges involved in composting are GHG emissions and energy requirements [5,6]. Therefore, other options for fallen leaf management, according to the idea of a circular economy, are investigated. Fallen leaves are studied as a resource for production of biochar [7] and biohydrogen [8,9]. Carbonized fallen leaves are used in solar–thermal evaporators for water desalinization [10]. Fallen Ginkgo leaves are used to produce medium-chain fatty acids via their co-fermentation of antibiotic fermentation residues [11].

Fallen leaves can also be used as a feedstock in biogas production. Anaerobic digestion (AD) is a biological process involving the decomposition of organic matter in anaerobic conditions, yielding biogas as the main product, which is used for energy generation, and a digestate as the byproduct, commonly used as fertilizer. Organic material can be processed as a single type in mono-digestion systems or as multiple types in co-digestion systems. Co-digestion is now more preferred since various types of feedstock digested together provide proper carbon-to-nitrogen (C/N) ratio, alkalinity, total solids (TS), and pH to effective biogas production [12]. The AD process can operate at various TS contents, depending on the feedstock and process design [13]. Therefore, the AD technology can be classified based on TS content as wet or liquid-state AD, also referred as low-solid system, and dry or solid-state AD, also referred as high-solid [13–16]. Wet systems operate at TS $< 15\%$, usually below 10%, and dry systems have TS $> 15\%$ [17], commonly in the range of 20–40% [18]. More detailed classification includes wet AD (TS $< 10\%$), semi-dry AD ($10\% <$ TS $< 15\%$), and dry AD (TS $\geq 15\%$) technologies [19,20]. Wet technology often requires additional liquid, e.g., water or recirculated liquid digestate, to reduce the dry matter of the mixture, mixing equipment, pumps, and agitators, and produces digestate with low dry matter. On the contrary, the dry AD technology requires lower power and heat, a low amount of liquid, and less maintenance since the system is less complex with less critical equipment, such as pumps, agitation systems, and feeding systems, comparing to wet AD systems. Dry AD offers advantages such as more favorable energy balance and better flexibility [21–26]. However, in dry technology, the increasing TS content leads to a reduction in methane (CH_4) content in biogas due to the increase in volatile fatty acids (VFAs) and decrease in pH [14,27,28]. Dry AD system performance is limited by thickness and diffusion, leading to the local accumulation of hydrogen (H_2) and VFAs [28].

Several studies on biogas production from fallen leaves of different species have reported various results depending on leaf freshness, species, and AD technology. The CH_4 yield from mono-digestion of Oxytree (Paulownia) ranged from 172 m^3 $Mg_{VS}{}^{-1}$ to 223 m^3 $Mg_{VS}{}^{-1}$, depending on the time of leaf collection [29]. The CH_4 concentration in biogas produced from semi-dried banana leaves was ca. 62% [30].

Recent studies on biogas production from fallen leaves have revealed that this material has potential as a feedstock, mainly in co-digestion. Mono-digestion of fallen leaves resulted in a biogas yield of 63.13 m^3 Mg^{-1} and was lower than the biogas yield from potato peelings and maize waste [31]. Solid-state mono-digestion of fallen leaves resulted in lower biogas production than co-digestion of straw and leaves at a ratio of 2:1 [32]. Similar results were reported by Rouf et al. [33], who investigated the mono-digestion of pre-treated and raw fallen leaves, and co-digestion of leaves with cow dung. In turn, the best results from co-digestion of fallen leaves, fruit, and vegetable wastes with cow dung were obtained when the fallen leaves-to-waste mixing ratio was 40:60 [34]. The co-digestion of fallen leaves, grass, and primary sludge performed the best at a C/N ratio of 13, while the highest CH_4 content was produced at an OLR of 1.0 g_{VS} L^{-1} d^{-1} [35]. The addition of 30% (on dry matter) of fallen leaves to poultry litter reduced the lag phase and intensified CH_4 production [36], and co-digestion of neem leaf litter with vegetable waste reduced formation of hydrogen sulfide (H_2S) and enhanced CH_4 production [37]. Co-digestion of food waste with rain tree leaves at a ratio of 95:5 increased CH_4 production [38]. Fallen leaf pre-treatment enhanced the CH_4 yield in dry AD [39]. Pre-treatment of teak fallen leaves and microalgae led to higher biodegradability of TS, volatile solids (VS), and chemical oxygen demand (COD), along with biogas and CH_4 yields, in comparison with mono-digestion [40]. In the case of fallen leaves, both wet and dry AD technologies are used. However, there is a gap in knowledge about the comparison of CH_4 production from fallen leaves in both technologies.

The aim of this study is comparison of mono-digestion of fallen leaves from three tree species in wet and dry AD systems. The tree species, namely, northern red oak (*Quercus rubra* L.), small-leaved lime (*Tilia cordata* Mill.), and Norway maple (*Acer platanoides* L.), are very common in Polish cities [41]. This study will give an insight into the CH_4 potential of fallen leaves from tree species in both wet and dry AD technologies. The main novelty of this study lies in the comparison of methane yields from fallen leaves produced using two AD technologies, namely, wet AD and dry AD. This research fills a gap in knowledge concerning the mono-digestion of fallen leaves from three common tree species, thereby this research advances the knowledge on biogas production from this feedstock. These finding provide biogas plant operators with valuable insights into the feasibility of using fallen leaves for energy generation.

2. Materials and Methods

2.1. Substrates and Inoculum

CH_4 potential tests in wet and dry AD technology were performed on fallen leaves from trees growing in Białystok and its vicinity (53°07′ N, 23°09′ E, 136 m a.s.l.). Białystok is located in the northeastern part of Poland. The region is characterized by a temperate climate with continental influences, with an average annual temperature of 7.6 °C (1995–2019) and an average annual precipitation of 608 mm (1995–2019) [42]. The samples were collected in autumn from three tree species planted commonly in parks and along streets: northern red oak (*Quercus rubra* L.), small-leaved lime (*Tilia cordata* Mill.), and Norway maple (*Acer platanoides* L.).

The digestate from a mesophilic agricultural biogas plant fed with maize silage and supplemented with 10–20% of food and farming wastes was used as inoculum. After delivering to the laboratory, the digestate used for the wet AD experiment was degassed at 38 °C. The inoculum was characterized with TS content of 5.00 ± 0.05% and VS content equal to 76.06 ± 0.58% TS. The digestate used for the dry AD experiment was degassed and then centrifuged at 3500 rpm for 30 min. The liquid fraction was discarded, and the solid part was used in the experiment. The main properties of solid part of inoculum were as follows: TS content 10.39 ± 0.29% and VS content 78.78 ± 0.55% TS.

2.2. Biochemical Methane Potential (BMP) Tests and Calculations

In wet AD technology, a BMP test of three substrates was conducted in batch assay in eudiometers with a volume of 1 L and a working volume of approximately 300 mL (Figure 1). The reactors were incubated at the temperature of 38 ± 1 °C in a water bath. This temperature is commonly used in biogas plants since the optimal temperature for the majority of species of the methanobacteria family is between 37 °C and 40 °C [43]. The substrates and inoculum were added to the reactors in a ratio of 2:1 based on VS content. The addition of distilled water set TS in the reactors equal to 5%. To maintain anaerobic conditions, the reactors were subjected to a 2 min flush with nitrogen. The BMP test for every substrate was performed in triplicate. Three reactors filled with inoculum and distilled water were used as control.

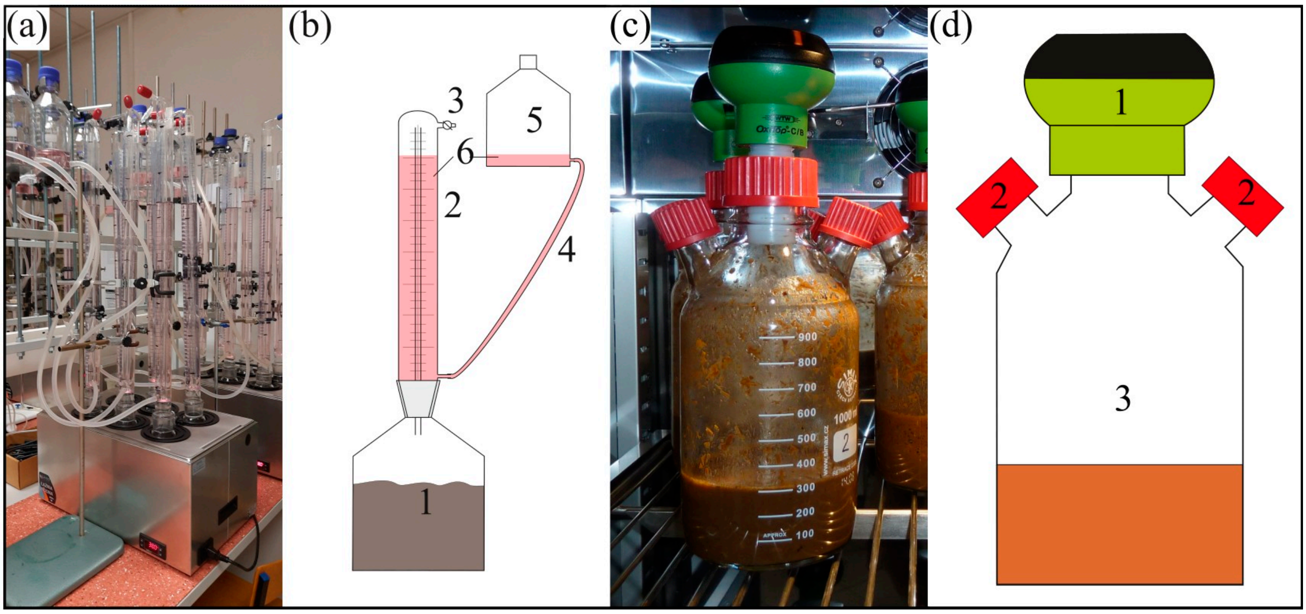

Figure 1. The BMP experiment: (**a**) Eudiometer sets in water bath. (**b**) The eudiometer set: 1—glass bottle (reactor) with mixture of inoculum and substrate; 2—the eudiometer tube with internal glass tube for gas transport; 3—valve for gas sampling; 4—connecting tube; 5—pressure compensation reservoir; 6—confining liquid. (**c**) OxiTop® reactor in thermostatic cabinet. (**d**) OxiTop® reactor: 1—measuring head; 2—side connectors; 3—reactor with mixture of inoculum and substrate.

In dry AD technology, the OxiTop® reactors (WTW, Weilheim, Germany) were incubated in a thermostatic incubator at 38 ± 1 °C to conduct the BMP test. The substrates and inoculum were added to the reactors in a ratio of 1:1 based on VS content. The TS content in reactors was 17%. To maintain anaerobic conditions, the reactors were flushed with nitrogen for 2 min. The BMP tests were performed in triplicate, along with three control reactors filled solely with inoculum.

In eudiometers, the biogas production was measured by volumetric method. In the OxiTop® reactors, biogas production was monitored at intervals of 240 min based on pressure changes within the reactor, facilitated by the OxiTop® measuring head (Figure 1). In both experiments, the composition of the biogas was analyzed using the portable biogas analyzer DP-28BIO (Nanosens, Wysogotowo, Poland). In wet AD, biogas samples were collected through a valve for gas sampling when the eudiometer tube was fully filled with biogas, just prior to realizing the gas. In dry AD, samples were taken with 20 mL gas-tight glass syringes when measuring head indicated the need to release gas (Figure 1). In the beginning of the experiments, the biogas composition was measured daily, transitioning to twice a week after the experiment had run for 10 days. The batch test was conducted until the daily CH_4 production was less than 1% of the total cumulative volume of CH_4 observed over three consecutive days [44].

The total cumulative CH_4 yield was calculated at the end of the BMP test. To calculate the specific methane yield (SMY) of each sample, the CH_4 produced from the inoculum was subtracted from the CH_4 produced by each sample. SMY was then given as NL CH_4 $kg_{VS}{}^{-1}$ according to the ideal gas law and to the molar volume of ideal gases at standard temperature and pressure conditions (NL = normal liter, i.e., gas volume corrected to 0 °C and 1013 bar). The kinetics of CH_4 production was determined using the modified Gompertz model, which is commonly used to show relationship between cumulative gas production and fermentation time:

$$G(t) = G_0 \times exp\{-exp\left[\frac{R_{max} \times e}{G_0}(\lambda - t) + 1\right]\}$$

where:

- $G(t)$—cumulative CH_4 production at specific time t (mL);
- G_0—CH_4 production potential (mL);
- R_{max}—maximum CH_4 production rate (mL day^{-1});
- λ—duration of lag phase (minimum time to produce CH_4) (days);
- t—cumulative time for CH_4 production (days);
- e—mathematical constant (2.71828).
- The modified Gompertz model allows for estimating the biogas production potential, together with the maximum biogas potential rate and the lag phase [45].

2.3. Analytical Methods

The samples were characterized in terms of TS, VS, pH, electrical conductivity (EC), total Kjeldahl nitrogen (TKN) content, total phosphorus (TP) content, potassium (K) content, and total organic carbon (TOC) content. The TS content was obtained by drying material to constant weight at 105 ± 2 °C, and the VS content was determined after incineration of dried material at 550 °C for 6 h in a muffle furnace according to standard methods [46]. A digital HQ40D meter (Hach, Loveland, CO, USA) was used to quantify the pH level and EC in 1:10 substrate/water suspension. In fresh samples, TKN, which is the sum of organic nitrogen and ammonia nitrogen [46], was determined by the Kjeldahl method in a Vapodest 50 s analyzer (Gerhardt, Königswinter, Germany). The oven-dried and ground samples were conducted to nitric acid/hydrogen peroxide microwave digestion in an ETHOS One (Milestone s.r.l., Milan, Italy). In digested samples, the content of TP was determined with ammonium metavanadate method using a UV-1800 spectrophotometer (Shimadzu, Kyoto, Japan) and the content of K was analyzed using flame photometry (BWB Technology, Newbury, UK). TOC content was measured in a TOC-L analyzer with an SSM-5000A Solid Sample Combustion Unit (Shimadzu, Kyoto, Japan). All analyses were run in triplicate, and all results are presented on a dry weight basis. In the case of fallen leaves from *Quercus rubra* and *Tilia cordata*, the TS was measured only in one sample due to equipment failure.

2.4. Statistical Analyses

Significant differences in cumulative CH_4 production among substrates in each technology and chemical composition of substrates were assessed with one-way variance analysis (ANOVA; single factor). The homogeneity of variance and normality were checked prior to ANOVA using the Levene and Shapiro–Wilk tests, respectively. Multiple mean comparisons were carried out with Tukey's honest significant difference (HSD) test. Significant differences in cumulative CH_4 production between technologies were assessed with Student' t-test. The level of accepted statistical significance was $p < 0.05$. All the statistical analyses of data were performed using STATISTICA 13.3 software (TIBCO Software Inc., Palo Alto, CA, USA).

3. Results

3.1. Feedstock Characteristics

The highest TS was observed in the leaves of *Quercus*, with lower TS found in both other species (Table 1). The VS content was also the highest in *Quercus* and significantly lower ($p < 0.05$) in *Tilia* and *Acer*. The EC and K content were similar in the leaves of *Quercus* and *Tilia* and differed significantly ($p < 0.05$) from *Acer*. TKN content and P content differed significantly ($p < 0.05$) among all three species, while TOC content was similar in *Quercus* and *Acer*. The differences in TKN, TOC, and TP content resulted in a high C/N ratio in fallen leaves of *Quercus* and *Acer* and a much lower C/N ratio in *Tilia*. Regarding the N/P ratio, the lowest value was calculated for *Acer* and the highest for *Quercus* (Table 2).

Table 1. Total solids, volatile solids, and pH (means ± SD, *n* = 3) of fallen leaves from three tree species.

Substrates	Total Solids (TS)	Volatile Solids (VS)	Electrical Conductivity (EC)	pH
	%	%TS	mS cm^{-1}	
Tilia cordata Mill.	62.46	82.85 ± 1.90 ab	7.25 ± 0.01 a	7.36 ± 0.01 a
Quercus rubra L.	91.85	90.87 ± 0.75 a	7.28 ± 0.06 a	7.31 ± 0.01 a
Acer platanoides L.	70.99 ± 3.46	82.16 ± 5.51 b	7.60 ± 0.04 b	7.32 ± 0.03 a

Table 2. Chemical composition (means ± SD, *n* = 3) of fallen leaves from three tree species.

Substrates	Total Kjeldahl Nitrogen (TKN)	Total Phosphorus (TP)	Total Potassium (K)	Total Organic Carbon (TOC)	C/N	N/P
	g $kg_{DM}$$^{-1}$					
Tilia cordata Mill.	12.98 ± 0.19 b	2.31 ± 0.22 b	4.96 ± 0.23 a	475.67 ± 2.43 b	37	6
Quercus rubra L.	9.80 ± 0.47 a	1.06 ± 0.14 a	5.27 ± 0.04 a	500.50 ± 7.16 a	51	9
Acer platanoides L.	7.30 ± 0.05 c	4.69 ± 0.45 c	13.37 ± 0.38 b	496.43 ± 2.11 a	68	2

Lowercase letters indicate statistical differences at $p < 0.05$.

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3.2. SMY of Fallen Leaves

In wet AD technology, the highest SMY (115.69 ± 4.11 NL kg_{VS}^{-1}**)** was found for *Quercus* leaves, with a lower SMY, though not significantly so, observed for *Acer* leaves (Table 3). A significantly lower ($p < 0.05$) SMY was found for *Tilia* leaves. In dry AD technology, the lowest SMY was also observed for *Tilia* leaves (55.23 ± 3.36 NL kg_{VS}^{-1}), while the highest SMY was observed for *Acer* (108.22 ± 2.02 NL kg_{VS}^{-1}).

Table 3. Specific methane yield (means ± SD, *n* = 3) of fallen leaves from three tree species in dry and wet anaerobic digestion.

Substrates	Wet Anaerobic Digestion	Dry Anaerobic Digestion
	NL kg_{VS}^{-1}	
Tilia cordata Mill.	56.80 ± 1.34 bA	55.23 ± 3.36 bA
Quercus rubra L.	115.69 ± 4.11 aA	98.49 ± 3.15 aB
Acer platanoides L.	107.52 ± 4.46 aA	108.22 ± 2.02 cA

Lowercase letters indicate statistical differences at $p < 0.05$ among SMY from three substrates in dry and wet AD separately. Uppercase letters indicate statistical differences at $p < 0.05$ among SMY from one substrate in dry and wet AD.

Comparison of SMY, according to technology, revealed that in the case of *Tilia* and *Acer* leaves the TS in the system had no influence on CH_4 production. SMY produced from *Quercus* leaves was significantly higher ($p < 0.05$) in the wet AD than in the dry AD system (Figure 2).

In both systems, the CH_4 content in biogas was very similar and ranged from 53% to 56%. The lowest CH_4 content was observed for *Acer* leaves in both systems while the highest CH_4 content was found for *Tilia* in both AD technologies.

In wet AD, the daily CH_4 production followed a similar pattern for all three species (Figure 3). The first peak was observed on day 1, followed by a decrease on day 2. The highest peak occurred on days 3 and 4. *Acer* leaves produced 9.3 NL kg_{VS}^{-1} d^{-1} on day 4, *Quercus* leaves produced ca. 5 NL kg_{VS}^{-1} d^{-1} over days 3 and 4, while *Tilia* peaked only to 2.80 NL kg_{VS}^{-1} d^{-1}. On days 10 to 12, the CH_4 production from all three species was very low, ranging from nearly 0 NL kg_{VS}^{-1} d^{-1} for *Tilia* leaves to ca. 1 NL kg_{VS}^{-1} d^{-1} for *Acer* and *Quercus* leaves. This decrease was followed by an increase to 1.68–3.32 NL kg_{VS}^{-1} d^{-1}, after which low but stable CH_4 production was observed. A second short decrease was noted on day 40 during AD of *Quercus* leaves, when CH_4 production fell to 0.44 NL $kg_{VS}{}^{-1}$ d^{-1}. The decreases noted during the AD of *Acer* and *Tilia* leaves were longer and lasted from day 35 to day 41. From that point until the end of the experiment, the daily CH_4 production in the AD of all three species stable and below 2 NL $kg_{VS}{}^{-1}$ d^{-1}.

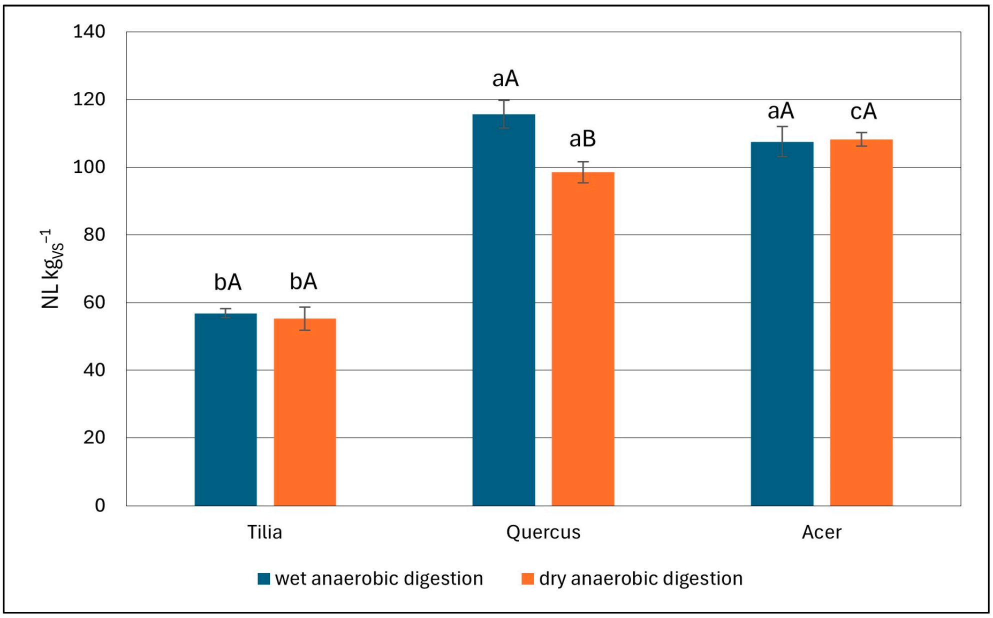

Figure 2. Specific methane yield (means ± SD, *n* = 3) of fallen leaves from three tree species in dry and wet anaerobic digestion. Lowercase letters indicate statistical differences at $p < 0.05$ among SMY from three substrates in dry and wet AD separately. Uppercase letters indicate statistical differences at $p < 0.05$ among SMY from one substrate in dry and wet AD.

In contrast, the daily CH_4 production patterns differed for all three species during dry AD (Figure 4). CH_4 production form *Acer* started with the peaks on days 1 and 2. These two peaks were the maximum CH_4 production during the dry AD of *Acer* leaves, reaching 6.81 and 7.13 NL $kg_{VS}{}^{-1}$ d^{-1}. Over the following days, production rapidly decreased to 2.46 NL $kg_{VS}{}^{-1}$ d^{-1} and remained stable until day 22, from which a gradual decline in CH_4 production was observed until the end of experiment. In contrast, the dry AD of *Quercus* leaves started with a much smaller peak on day 3, followed by a decline and a significant peak on day 8, reaching a maximum daily production of 8.60 NL $kg_{VS}{}^{-1}$ d^{-1}. This highest peak was followed by a rapid decrease and two much smaller peaks of 5.23 NL $kg_{VS}{}^{-1}$ d^{-1} and 3.77 NL $kg_{VS}{}^{-1}$ d^{-1} on days 13 and 16, respectively. From day 16, a slow decline in daily CH_4 production was observed until the end of the experiment. The pattern of daily CH_4 production during the dry AD of *Tilia* was the most even. CH_4 production gradually increased, reaching a maximum of 4.01 NL $kg_{VS}{}^{-1}$ d^{-1} on day 11. A slow decline in daily CH_4 production was then observed until the end of the experiment.

The highest daily maximum production from *Acer* leaves resulted in the best performance in cumulative CH_4 production until day 38. Even though the maximum daily CH_4 production during wet AD of *Quercus* reached only half of that from *Acer*, the higher daily production of CH_4 throughout almost entire stable phase of the wet AD process for *Quercus* resulted in higher cumulative CH_4 production from the whole process (Figure 5).

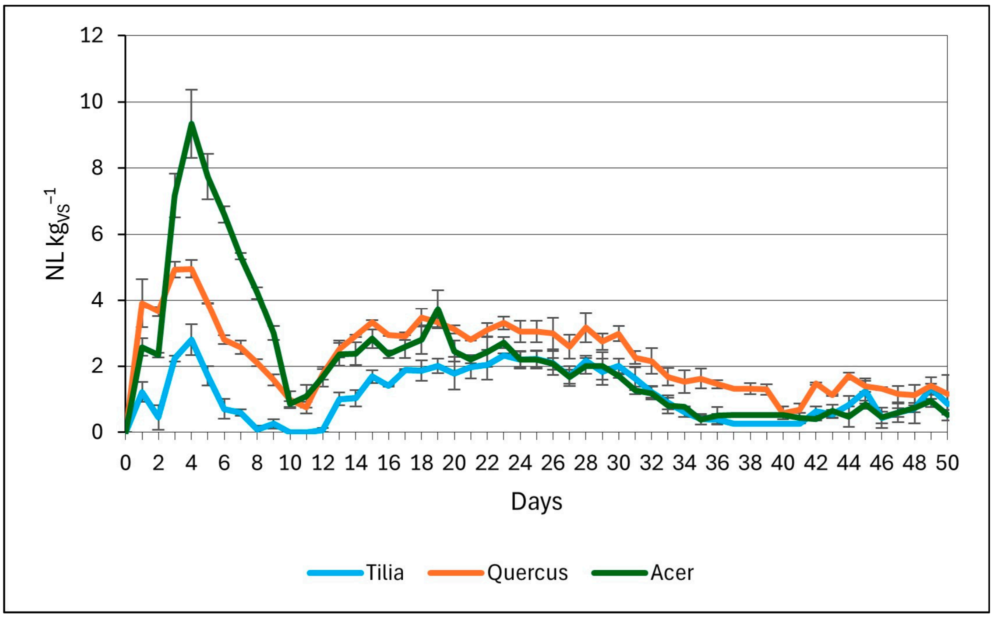

Figure 3. Daily methane production in wet anaerobic digestion technology from fallen leaves of three tree species. Standard errors are shown as vertical bars.

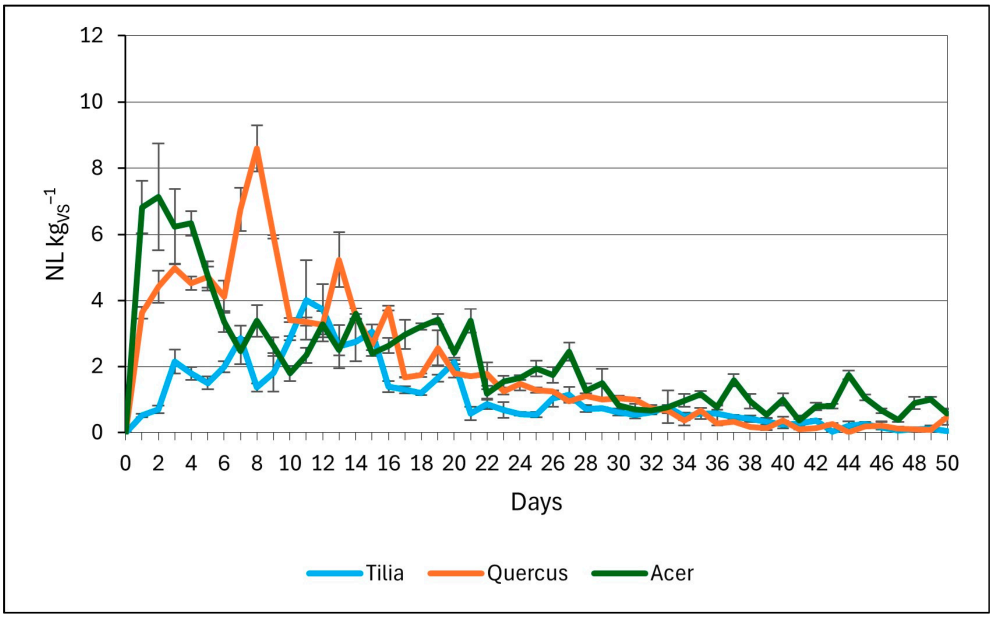

Figure 4. Daily methane production in dry anaerobic digestion technology from fallen leaves of three tree species. Standard errors are shown as vertical bars.

The opposite situation was observed during dry AD. In this technology, the highest maximum daily CH_4 production for *Quercus* leaves, but daily CH_4 production from *Acer* leaves remained higher throughout most of the stable AD phase. Therefore, even though cumulative CH_4 production was higher for *Quercus* from day 8 to day 34, the final cumulative CH_4 production at the end of the experiment was higher during dry AD of *Acer* leaves (Figure 6).

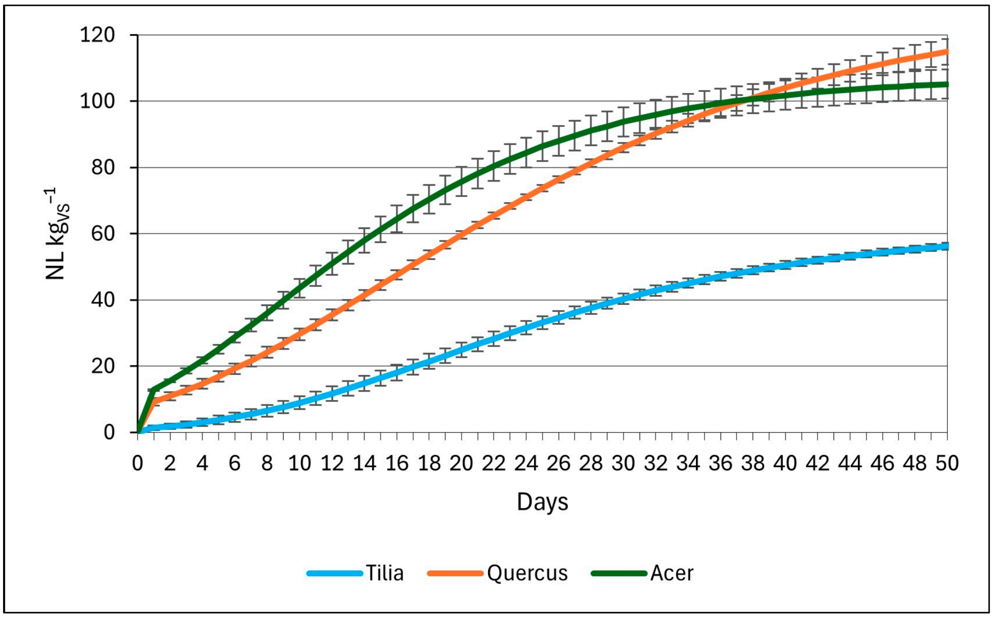

Figure 5. Cumulative methane production in wet anaerobic digestion technology from fallen leaves of three tree species. Standard errors are shown as vertical bars.

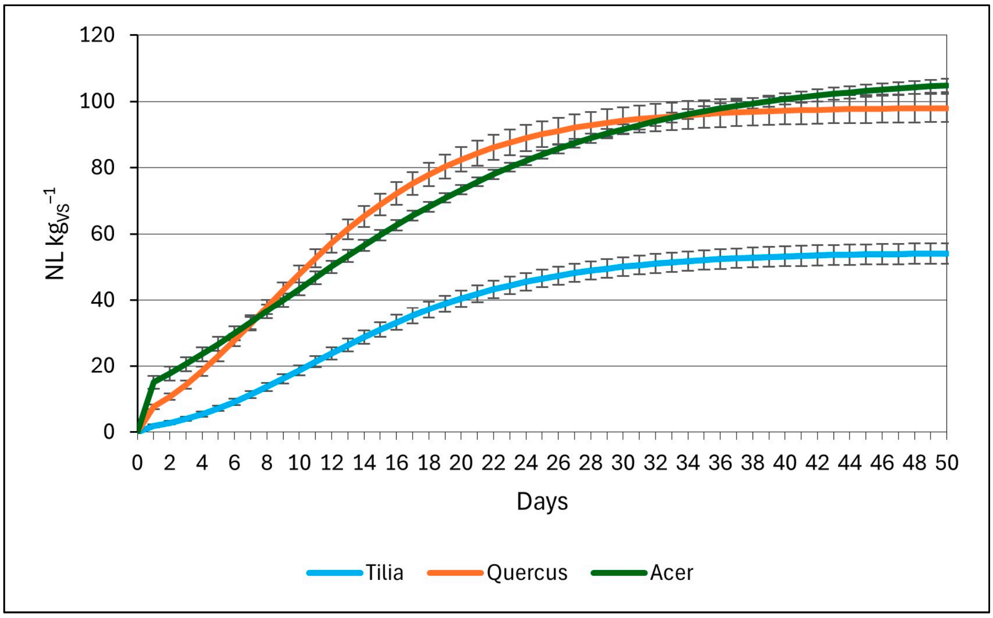

Figure 6. Cumulative methane production in dry anaerobic digestion technology from fallen leaves of three tree species. Standard errors are shown as vertical bars.

In both technologies, the worst performance was observed in the case of *Tilia* leaves. Low daily CH_4 production without significant peaks resulted in low cumulative CH_4 production, with long lag phase of 20 days in wet AD and 10 days in dry AD.

High stability of the AD process is one of the main challenges in biogas plants. Process disturbances or even termination may be caused by several factors, such as the process-related accumulation of inhibitors, e.g., ammonia (NH_3) and hydrogen sulfide (H_2S) [47]. In this study, in wet AD technology, the highest NH_3 concentration was observed in the case of *Acer* leaves (Figure 7). After two days of wet AD, the NH_3 concentration increased to a maximum value of 145.7 ppm on day 7, then slowly decreased to 65.6 ppm by day 50. In contrast, wet AD of *Tilia* and *Quercus* produced biogas with very low NH_3 concentrations, which gradually increased from day 5, starting at zero ppm and reaching 11.4 ppm and 21.7 ppm, respectively, on day 50.

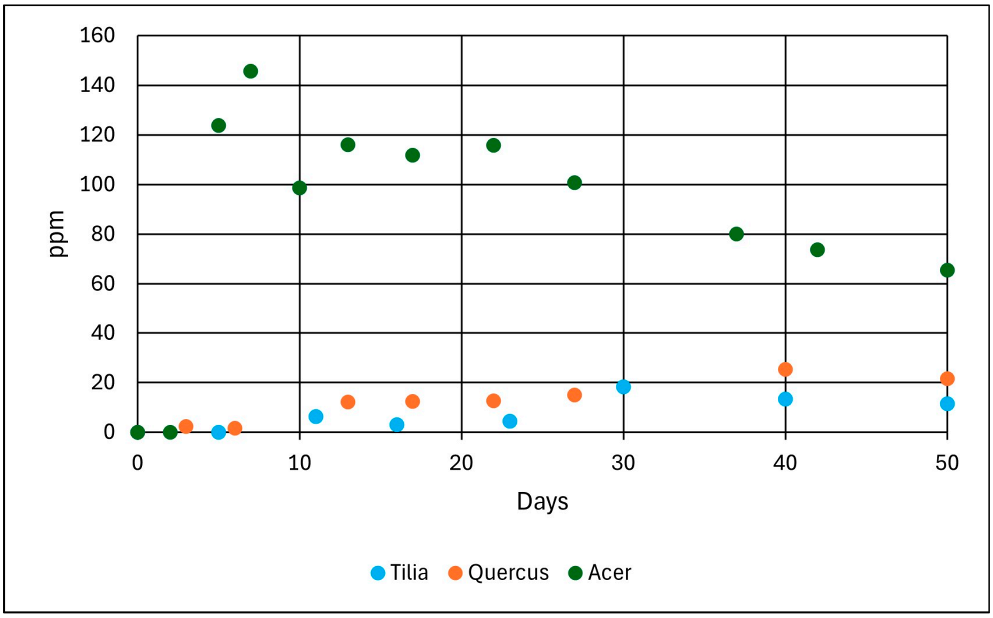

Figure 7. Concentration of the ammonia in biogas produced in wet anaerobic digestion technology from fallen leaves of three tree species.

A similar pattern of H_2S concentration to that of NH_3 was observed. The highest H_2S concentration throughout the process was recorded in biogas produced from *Acer* leaves. The H_2S concentration increased after 5 days and reached a maximum value of 889.7 ppm on day 7 (Figure 8). After a week, the H_2S concentration started to decrease slowly to 667.4 by day 50. In biogas produced from *Tilia* and *Quercus* leaves, the H_2S concentration remained very low, only starting to increase from day 10, reaching a maximum of 200.3 ppm for *Quercus* and 115.1 ppm for *Tilia* leaves by day 50 at the end of the experiment.

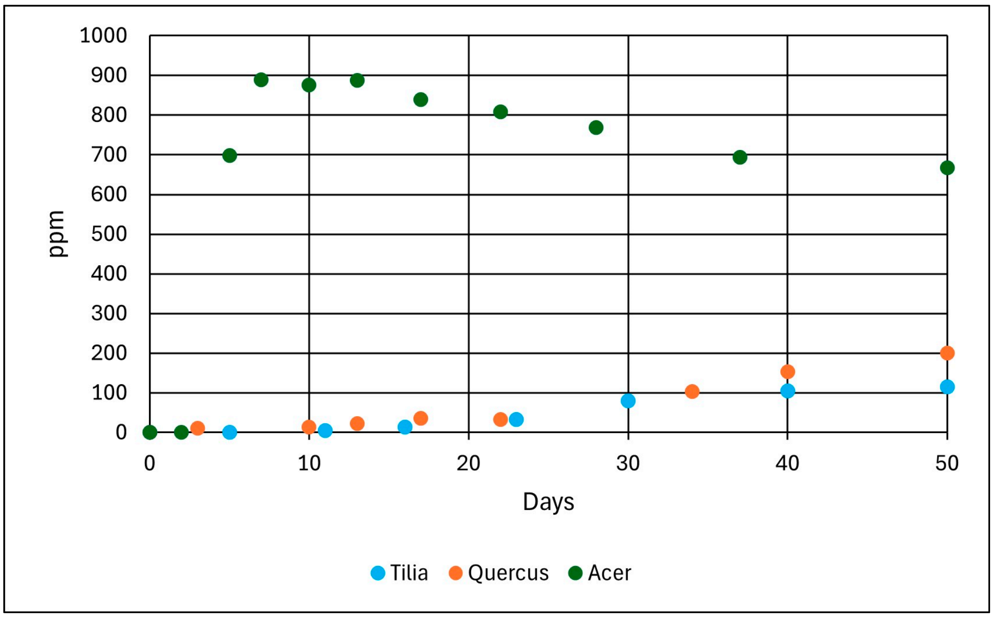

Figure 8. Concentration of hydrogen sulfide in biogas produced in wet anaerobic digestion technology from fallen leaves of three tree species.

In dry AD, the NH_3 concentration in biogas produced from *Acer* leaves was the highest throughout the entire experiment (Figure 9). The NH_3 concentration peaked to maximum value (208.9 ppm) on day 4 and then decreased gradually to 32.0 ppm by the end of the experiment. Concentrations of this inhibitor in biogas from *Tilia* and *Quercus* were negligible throughout 50 days of experimentation.

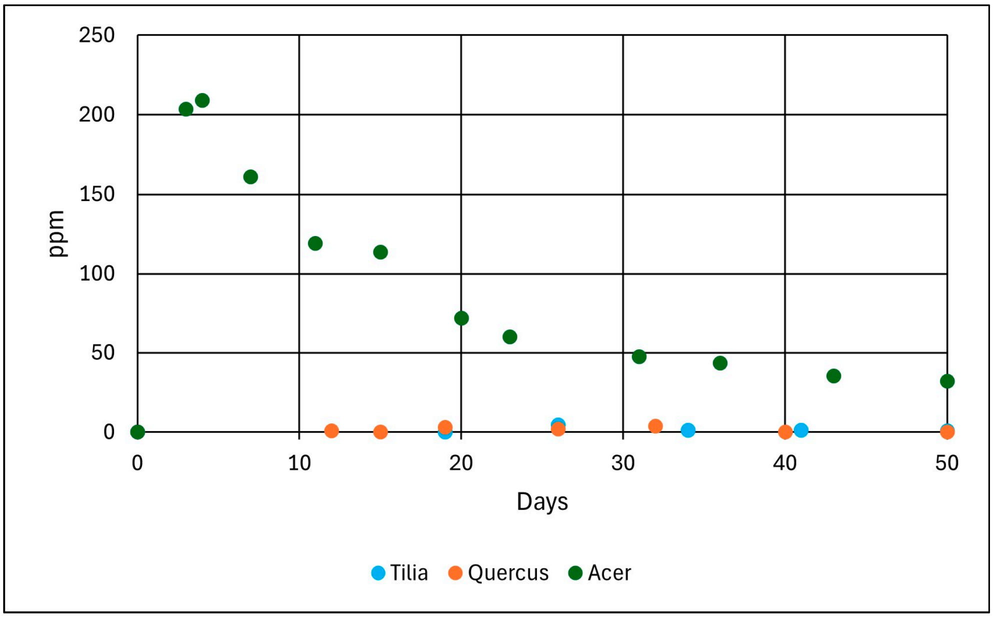

Figure 9. Concentration of the ammonia in biogas produced in dry anaerobic digestion technology from fallen leaves of three tree species.

H_2S concentration in biogas produced from *Acer* leaves was also much higher than that in biogas produced from *Tilia* and *Quercus* leaves (Figure 10). The maximum H_2S concentration was observed on day 4 and was equal to 1279.8 ppm. In the subsequent days, the H_2S concentration declined to 267.4 ppm. In biogas produced from *Tilia* and *Quercus* the H_2S concentration remained close to zero.

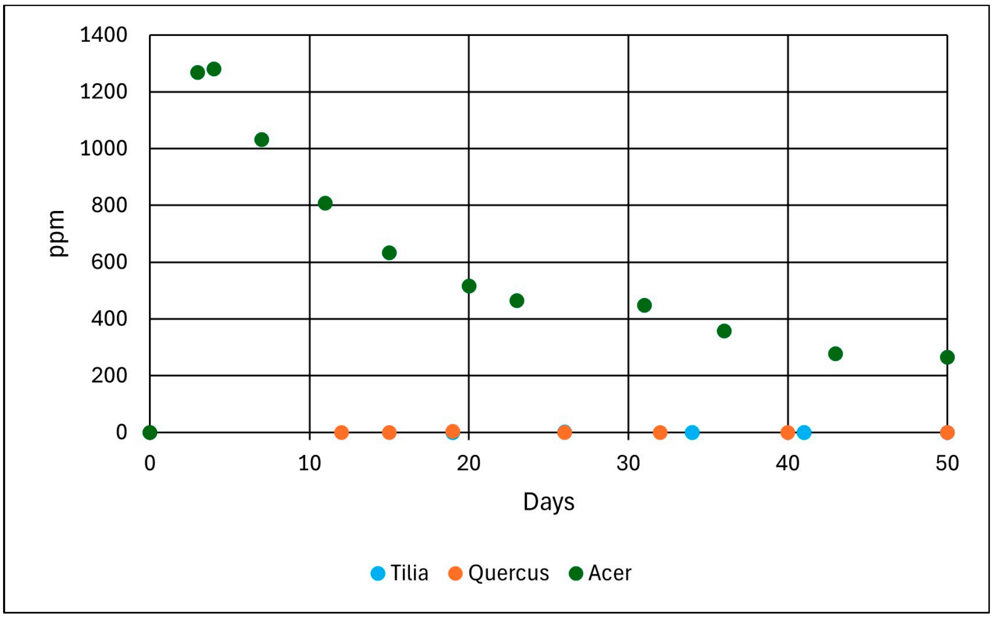

Figure 10. Concentration of hydrogen sulfide in biogas produced in dry anaerobic digestion technology from fallen leaves of three tree species.

4. Discussion

The seasonal leaf senescence in the phenological cycle prepares trees for winter dormancy. The autumn leaf senescence triggers transition in cellular metabolism and degradation of cellular structures. Breakdown of chlorophylls, increase in lipid peroxidation, and membrane leakiness are the main symptoms of this process. In this stage, proteins, lipids, nucleic acids, and pigments are hydrolyzed, and nutrients from degraded macromolecules are relocated to stems and roots in trees [48]. Thus, the nutrient content in fallen leaves is rather low, while TS and VS contents are high. In this study, TS content ranged from 62.46% in *Tilia* leaves to ca. 71% in *Acer* leaves. High TS content, up to 98%, was observed in fallen leaves of teak [40]. Fallen leaves from mahogany, eucalyptus, and rain tree were characterized by a TS content of 88.14% [33]. The TS content of *Quercus robur* leaves, equal to ca. 95%, was reported by Killic et al. [49]. The TS content of fallen leaves from the studied species was higher than that noted for the same species in Berlin [50]. The VS content in the studied species was in the range of 82–91%TS and was similar to this parameter reported in other studies [33,40,50].

Nutrient content in fallen leaves depends on several factors. Low nutrient content may be the result of their movement from leaves to stems and roots during leaf senescence [48]. Low nutrient content may result from low uptake and storage under challenging environmental conditions. Trees growing along streets are often exposed to various stressful conditions. Their growth is often determined by the limited soil volume, which leads to nutrient depletion. Fallen leaf raking disrupts the nutrient cycle by limiting organic matter decomposition. This lack of organic matter, along with the absence of decomposers such as invertebrates and microorganisms, leads to soil compaction, which in turn reduces the oxygen in soil. Under such environmental conditions, chlorophyll content in tree leaves may be reduced [51]. Another challenge is increased EC and excessively high soil pH, which limits the availability of many minerals [52]. As a result, biomass production and nutrient accumulation in leaves may be much lower. Malinowska [53] reported reduced K content in leaves from *Acer* trees growing along the streets in Gdańsk and Gdynia, Poland compared to those growing in housing estates, parks, and control stand. Trees such as *Tilia cordata*, *Acer platanoides*, and *Quercus robur* are sensitive to salinity stress [54].

Fallen leaves of *Tilia* contained much less N (12.3 g ${kg_{DM}}^{-1}$) than fresh leaves, in which N content ranged from 30.8 g kg^{-1} to 73.1 g kg^{-1} [52,55]; however, studies of Marosz and Nowak [54] revealed that N content in fresh leaves was 14.4 g kg^{-1}. In turn, the N content in *Tilia* leaves from the present study was similar to the N content in fallen leaves collected in Berlin, Germany [50] and in leaf litter collected in Słupsk, Poland [56]. N content in *Quercus* fallen leaves was similar to values in fresh leaves obtained by Marosz and Nowak [54] and to leaf litter collected in Słupsk, Poland [56] but was higher than its content in fallen leaves in Berlin, Germany [50]. Fallen leaves of *Acer* contained 7.3 g N ${kg_{DM}}^{-1}$, which was lower than result shown by Vargas-Soplin et al. [50] and much lower than the N content in fresh leaves [52,54,57]. However, N content in the present study was similar to the result reported by Parzych et al. [56].

Tilia fallen leaves in this study contained 2.3 g P kg^{-1}, which was similar to the results obtained by Wilkaniec et al. [52] in fresh leaves and higher than the value reported by Marosz and Nowak [54]. P content in *Quercus* leaves was similar to the value reported by Marosz and Nowak [54], while P content in *Acer* fallen leaves was higher than values reported in the literature [52,54]. However, the P content in fallen leaves of three studied species was much higher than the concentration of this nutrient in leaf litter reported by Parzych et al. [56].

K content (5.0 g ${kg_{DM}}^{-1}$) in fallen leaves from *Tilia* was lower than values reported for fresh leaves (9.8–23.6 g kg^{-1}) [52,54,55] or leaf litter [56]. Fallen leaves of *Acer* and *Quercus* contained 5.3 g K ${kg_{DM}}^{-1}$ and 13.4 g K ${kg_{DM}}^{-1}$, respectively. Both values were lower than given in the literature for fresh leaves [52,54] but higher or similar to K content in fallen leaves reported by Mudryk [58]. However, Parzych et al. [56] reported higher values of K in freshly shed leaves.

The lower content of nitrogen, phosphorus, and potassium in fallen leaves compared to fresh leaves found in this study is likely due to the natural process of these nutrients being transported to the roots and stems as trees shed their leaves for winter [48]. Differences in the content of these nutrients compared to values reported in the literature [50,56] are related to the varied habitat conditions.

Carbon-to-nitrogen ratio is an important factor that shows the relationship between two main nutrients. The optimal C/N ratio in biogas production should lie within the range of 20 to 35 [16,59,60]; however, Dobre et al. [61] recommend a C/N ratio between 15 and 25. This ratio induces a low protein solubilization rate and leads to low total ammonia and VFA content, which in turn, may contribute to the prevention of ammonia inhibition. A higher C/N ratio reflects low nitrogen concentration, which, through fast degradation, may lead to insufficient biomass production, resulting in low biogas yield [38]. In this study, the C/N ratio ranges from 37 to 68. A high C/N ratio is typical for tree leaves [33,50,61]. Low TKN concentration with high carbon content results in rapid nitrogen consumption by methanogens. This leads to low biogas production [16]. The optimal N/P ratio in biogas production should be 3. Insufficient nutrient provision may impair the growth of anaerobic microbial species and thus inhibit or disturb the AD process [16,17]. In this study, the N/P ratio was almost optimal in the case of *Acer* leaves and too high in the case of *Tilia* and *Quercus* leaves. Leaf senescence is the final stage of development and nutrient relocation in trees [62]; thus, P and N concentrations may be low in fallen leaves.

In this study, the CH_4 production in the mono-digestion of fallen leaves was very low and ranged from 57 NL kg_{VS}^{-1} to 116 NL kg_{VS}^{-1} in wet AD technology and from 55 NL kg_{VS}^{-1} to 108 NL kg_{VS}^{-1} in dry AD system. SMY of studied species was much lower compared to the results obtained for AD of Oxytree leaves, which produced from 171 NL CH_4 kg_{VS}^{-1} to 222 NL CH_4 kg_{VS}^{-1} depending on the time of leaf collection. The highest SMY was obtained from growing leaves, and the lowest CH_4 yield was noted from leaves collected 1 week after falling [29]. The CH_4 yield from a substrate composed of fallen leaves of oak, maple, and birch was also higher than in the present study and was equal to 201 NL kg_{VS}^{-1} [63]. The CH_4 production from poplar tree leaves was also higher and was equal to 231 NL kg_{VS}^{-1} [64]. In turn, poplar waste used as a substrate in a dry AD system produced 81.1 NL CH_4 kg_{VS}^{-1} [65]. In wet AD of poplar waste, the CH_4 yield was affected by the concentration of the substrate and NaOH pre-treatment. CH_4 production decreased with increasing substrate concentration due to acidification of the anaerobic system. The highest SMY of untreated poplar waste was 127.2 NL kg_{VS}^{-1} [66], which is similar to the CH_4 yield obtained from *Quercus* leaves with wet AD technology in the present study. Pre-treatment of poplar waste with 5.0% NaOH increased CH_4 production to 271.9 NL kg_{VS}^{-1} [66].

The low methane yield obtained in this study could have been caused by several factors. The high TS content indicates an advanced process of leaf senescence, during which nutrient relocation occurred within the tree [48]. This, in turn, led to an imbalance in the C/N ratio and a reduction in the content of micro- and macronutrients in the studied fallen leaves. An improper C/N ratio, along with the lack or low content of macronutrients such as sulfur or nitrogen, may have caused low biogas production efficiency. The low SMY could also result from the presence of process inhibitors such as heavy metals [67] or polyphenols [68,69], which are broadly distributed in the plant kingdom and are the most abundant secondary metabolites of plants [70].

Fallen leaves have been used as a co-substrate in several studies [34,36,65,71]. The addition of 15% (on dry matter basis) of fallen leaves from *Acer platanoides* to poultry litter had no influence on biogas production, while the addition of 30% of leaves resulted in the maximum biogas yield. A further increase in the percentage of this additive had no impact on biogas production. Furthermore, the addition of fallen leaves reduced the lag phase of the AD of chicken manure [36]. In turn, the best performance of the co-digestion of fallen leaves with food waste and cow dung treated as an inoculum was obtained when the leaf-to-food waste ratio was 40:60. Co-digestion performance index confirms the synergistic effect of fallen leaves and food waste in AD only in this ratio. The highest SMY, equal to 98.2 NL $kg_{VS}{}^{-1}$, from poplar waste was obtained during co-digestion of this substrate with cattle slurry at a ratio of 1:1 with NaOH pre-treatment [65]. In turn, the CH_4 yield obtained from sugarcane leaves was 141 NL $kg_{VS}{}^{-1}$ and was slightly higher than the results presented in this study; however, the addition of food waste and cow dung resulted in much higher SMY, reaching 297 NL $kg_{VS}{}^{-1}$ [71]. Higher biogas yield from pre-treated fallen leaves co-digested with cow dung compared to untreaded and mono-digested leaves was also reported by Rouf et al. [33]. Similar results were reported by Wannapokin et al. [40] who co-digested with 2%NaOH pre-treated teak fallen leaves with algae and achieved ca. 72% higher yield than from mono-digestion.

Inhibition induced by NH_3 or H_2S is a frequent problem in AD systems, and dry AD is even more prone to accumulation of NH_3 and VFAs. During the stage of hydrolysis [72,73], degradation of N-containing compounds such as proteins, urea, and nuclide acids releases ammonium ions ($NH_4{}^+$), which stay in equilibrium with un-ionized ammonia (NH_3) [16,74–77]. This equilibrium depends on pH and temperature, and an increase in these parameters results in a higher release of NH_3 [77]. NH_3 easily diffuses through cell walls and causes proton imbalance, potassium deficiency, changes in intracellular pH, an increase in maintenance energy requirements, inhibition of specific enzyme reactions, and a CH_4 synthesizing system [16,59,60,77]. Thus, methanogens are particularly affected by NH_3 concentrations over 1800 ppm [59,74,77]. However, NH_3 concentration of 200 ppm is beneficial for AD since N is an essential nutrient for microorganisms [78]. Theuerl et al. [47] recommend NH_3 concentration in the range of 80–400 ppm. In this study, the optimal NH_3 concentration was observed only in biogas produced from *Acer* leaves in the beginning of the experiment. Low N content in leaves resulted in too low an NH_3 concentration to be beneficial for anaerobic microorganisms. A significantly higher concentration of NH_3 in biogas derived from *Acer* leaves may be attributed to an increase in pH during the AD process, which contributes to the elevated presence of molecular ammonia in biogas [74,78]. The rise in pH could be associated with the distinct chemical composition of Acer leaves, as indicated by their significantly higher P and K contents, as well as a significantly higher EC.

Sulfur is a particularly crucial element for methanogenic bacteria [58]; however, a high concentration of H_2S may inhibit the AD process since H_2S can diffuse into the cell membrane and denature native proteins through the formation of sulfide and disulfide cross-links between polypeptide chains [74,78]. This toxic sulfide is a product of the decomposition of sulfur-containing compounds such as amino acids, sulfoxides, and sulphonic acids. H_2S in biogas is also a product of the biological reduction of sulphates in the feedstock [74]. H_2S is not only toxic to anaerobic microorganisms but also, together with water present in biogas, forms corrosive condensate, which can damage a combined heat and power (CHP) units and pipes [78,79]. Furthermore, the combustion of biogas containing H_2S releases sulfur oxides (SOx) into the atmosphere [79,80], which can harm trees and plants by damaging foliage and decreasing growth, contributing to acid rains, and hurting the respiratory systems of living organisms. The threshold values for H_2S concentration depend on further biogas applications. Biogas upgraded for substitution of natural gas should not contain H_2S higher than 4–10 ppm [81], CHP units may operate with higher H_2S concentrations (100–500 ppm) [80,82], while biogas used in microturbines may contain up to 70,000 ppm [81]. In the present study, the highest H_2S concentration (ca. 1300 ppm) was observed only in biogas from *Acer* leaves. This concentration declined after 35 days to less than 400 ppm, which is an acceptable value for a CHP unit. In biogas from the two other substrates, the H_2S concentration was negligible. A significantly higher concentration of H_2S in biogas derived from *Acer* leaves might be attributed to elevated sulfur levels in this feedstock, as leaves were collected from greenery located along the streets. Although air quality in the European Union (EU) has improved significantly, data from the European Environment Agency (EEA) indicate that in urban areas of Poland, the annual mean concentration is between 5 and 10 $\mu g\ m^{-3}$, while in suburban areas, it is below 5 μg m^{-3}. However, Poland has recorded levels exceeding the EU daily limit value of 125 μg m^{-3} [83].

The concentration of NH_3 and H_2S below the threshold values suggests that, from this perspective, fallen leaves could serve as a suitable substrate or co-substrate for biogas production. However, it should be noted that such low concentrations of both inhibitors indicate very low N and S content. NH_3 concentration of ca. 200 ppm is beneficial for the AD process, as nitrogen is an essential nutrient for anaerobic microorganisms [78]. Consequently, insufficient nitrogen content, including in the form of NH_3, may reduce process efficiency. On the other hand, low sulfur content is favorable for biogas production.

Biogas production from fallen leaves presents an interesting and sustainable alternative to composting, aligning with the idea of sustainable development. Biogas from waste serves a source of green energy. Unlike energy generated from wind or photovoltaic panels, biogas production—and, consequently, energy production—remains stable throughout the year and is not dependent of weather conditions. However, to ensure the sustainability of biogas energy, the feedstock for production must be carefully chosen. Therefore, lignocellulosic waste, such as fallen leaves, mown grass, and similar materials, should be considered as substrates or co-substrates in biogas plants. The benefits and drawbacks of using fallen leaves as feedstock for biogas production are presented in Table 4.

Table 4. The benefits and drawback of anaerobic digestion of fallen leaves.

Benefits	Drawbacks
• Sustainable management of waste difficult to utilize • Reduction of GHG emissions due to avoidance of composting • Increase of generation of renewable energy • Provision of valuable fertilizer • Low content of inhibitors such as NH_3 and H_2S	• Low specific methane yield • Seasonality of feedstock • Feedstock difficult to storage due to natural degradation over time

This study revealed that SMY of *Tilia* and *Acer* were similar in both technologies; thus, selecting the optimal technology should be based on other criteria. Wet AD process is well developed and widely used; however, it has several disadvantages, including large reactor size, high costs, substantial processing water requirements, and a significant amount of digestate, whose post-treatment and disposal may pose challenges [20,21]. In contrast, dry AD offers several advantages such as smaller reactor size, easier digestate management, reduced processing water requirements, and lower operational costs [20–22].

5. Conclusions

Studies on the fallen leaves of *Tilia cordata*, *Quercus rubra*, and *Acer platanoides* as substrates in mono-digestion technology have shown their limited suitability for biogas production. However, this feedstock may serve as a co-substrate due to its low concentrations of NH_3 and H_2S, both of which are considered inhibitors in the AD process. Low concentrations of NH_3 and H_2S are unlikely to interfere with the AD of the main substrate in the biogas production process. Furthermore, the high dry matter content of fallen leaves suggests their potential role as a thickening agent for substrates with high water content. A comparison between two biogas production technologies revealed that, for *Tilia* and *Acer* leaves, the technology had no significant impact on CH_4 yield. In contrast, the wet AD of *Quercus* leaves resulted in significantly higher CH_4 production compared to dry AD technology. The current study provides only specific methane yield from three tree species in mono-digestion technology. Further studies should focus on co-digestion with various substrates to enhance methane yield, as well as investigate pre-treatment technologies.

Further study should aim to identify the optimal combination of pre-treatment parameters and the optimal conditions for anaerobic digestion. In addition, comprehensive research regarding the energy, economic, and environmental effectiveness are needed to analyze the use of fallen leaves as a feedstock for biogas production.

Author Contributions: Conceptualization, A.W.-C. and R.C.; methodology, A.W.-C. and R.C.; formal analysis, A.W.-C. and R.C.; investigation, A.W.-C. and R.C.; writing—original draft preparation, A.W.-C.; writing—review and editing, R.C.; visualization, A.W.-C. and R.C. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by the Ministry of Science and Higher Education as part of the project WZ/WB-IIŚ/3/2023.

Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of this study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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