biomass

MDPI

Article

Analysis of Biogas Component Production during Anaerobic Digestion of Sour Cabbage in Microaeration Conditions under Different pH Conditions

Gaweł Sołowski

Institute of Fluid-Flow Machinery of Polish Academy of Sciences, Fiszera 14st, 80-231 Gdansk, Poland; gawelsolowski@yahoo.com; Tel.: +48-58-6995-327

Abstract: Influences of following anaerobic digestion (AD) parameters like microaeration, pH, and VSS (Volatile Suspended Solid) using sour cabbage as substrate was checked in the publication. Results of fermentation of sour cabbage under the condition of small oxygen addition presented in this research can be classified as dark fermentation (DF—a special case of AD) or hydrogenotrophic anaerobic digestion. The investigations were carried out for two concentrations of 5 g VSS/L and 10 g VSS/L of sour cabbage at pH 6.0. The oxygen flow rates (OFR) for 5 g VSS/L were in the range of 0.53 to 3.3 mL/h for obtaining 2% to 8% of oxygen. At low pH and microaeration, ethylene production was observed at a level below 0.05% in biogas. The highest volume of hydrogen for 5 g VSS/L was obtained for flow rate 0.58 O_2 mL/h, giving hydrogen concentration in biogas in the range of 0 to 20%. For VSS 5 g/L and oxygen flow rate 0.58 mL/h; 0.021 L of hydrogen was produced per gram of VSS. At VSS 10 g/L and oxygen flow rate 1.4 mL/h at pH 6.0, 0.03 L of hydrogen was generated per gram. Microaeration from 0.58 mL/h to 0.87 mL/h was propitious for hydrogen production at 5 g VSS/L of sour cabbage and 1.4 mL/h for 10 g VSS/L. Another relevant factor is the volatile suspended solid factor of a substrate. Optimal hydrogen production from sour cabbage was for VSS 89.32%.

Keywords: volatile suspended solids; anaerobic digestion; hydrogen; sour cabbage; microaeration

Citation: Sołowski, G. Analysis of Biogas Component Production during Anaerobic Digestion of Sour Cabbage in Microaeration Conditions under Different pH Conditions. *Biomass* **2022**, *2*, 14–26. https://doi.org/10.3390/biomass2010002

Academic Editor: Paolo Defilippis

Received: 11 November 2021
Accepted: 27 December 2021
Published: 17 January 2022

1. Introduction

Dark fermentation (DF) is a kind of anaerobic digestion, where various organic substrates are converted into hydrogen, carbon dioxide, and low organic acids [1]. Anaerobic digestion (AD) is a 2–4 step process, but usually a 4-staged biological conversion of organic compounds to methane by anaerobic bacteria [2]. For the utilization of wastes, an AD is designed frequently [3]. Wastes, being (polysaccharides, fats proteins, or a complex combination of biopolymers like lignocelluloses), are hydrolyzed, then acidogenesis and acetogenesis. Low organic acids, carbon dioxide, and hydrogen are obtained in acidogenesis (in DF case process stops here). Then, in AD, hydrogen with carbon dioxide is converted into methane [4]. DF in an AD process is sometimes called hydrogenotrophic anaerobic digestion [5]. Produced in acidogenesis hydrogen, and carbon dioxide can increase methane yield in an AD, like in [6] or separated to obtain clean raw chemicals [7]. In dark fermentation, methane production, the ongoing process, should be inhibited to save the obtained hydrogen [8]. There is some disagreement if the dark fermentation process can 'officially' occur with unpretreated sludge if some hydrogen is still converted to methane production [9,10] or defined only as an anaerobic digestion case [11]. Then in the dark fermentation, there needs the stress of inoculum, resulting in biogas containing hydrogen and carbon dioxide [12]. Usually, in the DF process, bacterial sludge (inoculum) is stressed using heat (preheating or freezing) [13], ultrasound [14], or microwaves [15], centrifuging [16], chemicals [17], or change of pH [18]. Though works Lakaniemi et al. [10] and Li et al. [19] showed that untreated raw sludge could lead to hydrogen production

also. Most DF investigations state that optimal hydrogen production is in acidic pH [20]. Despite them, Li et al. [19] performed efficient hydrogen production from the cotton stalk by applying specific inoculum (carp intestine bacteria) in alkaline conditions. Therefore, the investigation of the optimal method of hydrogen production should explore an optimal range of pH for every substrate or mixture of substrates [21]. Another example of undesired dark fermentation with untreated inoculum is gangrene [22]. The not pretreated inoculum (allochthonous) resulted in high hydrogen production from grape waste [23]. Due to the optimal yield of dark fermentation, the process will probably be a stable supplemental method for other approaches to hydrogen production [24]. The next problem is a hydrogen sulfide formation [25] in anaerobic digestion [26] or composting at landfills [27]; the addition of small amounts of oxygen can prevent this formation. In earlier research was observed that in neutral pH, microaeration in dark fermentation of sour cabbage improved hydrogen production [28] like anaerobic digestion, enhanced methane production [29]. Thus, it seemed worth checking which process, hydrogenesis or methanogenesis, is more sensitive to oxygen presence. Microaeration of some range augmented dark fermentation of cotton wastes [30]. The addition of oxygen in the range from 2% to 8% in biogas helped with hydrogen production in photofermentation [31,32] and was called microaerobic DF [27]. The process of DF proceeds along with one of three possible pathways [33,34]. According to Bartacek et al. [33] and Woodward et al. [35], dark fermentation proceeds due to three thermodynamically possible reactions from hexoses: acetate Equation (1), butyrate Equation (2), and acetate-ethanol Equation (3):

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \quad (1)$$

$$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2 \quad (2)$$

$$C_6H_{12}O_6 + H_2O \rightarrow CH_3COOH + CH_3CH_2OH + 2CO + 2H_2 \quad (3)$$

The acetate pathway possesses the highest theoretical hydrogen yield: 4 moles of H_2 from a mole of hexose. The most efficient way is the acetate pathway (1) [36,37], but the most probable is the butyrate fermentation (2).

The methane production (if not inhibited) occurs from the acetogenesis like in [38], see Equations (4)–(6):

$$CO_2 + 4H_2 \rightarrow CH_4 + 6H_2O \quad (4)$$

$$CH_3CH_2CH_2COOH \rightarrow 2CH_4 + 2CO_2 \quad (5)$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad (6)$$

The dark fermentation pathways mentioned earlier omit some bottom products like lactic acid [39,40]. There is no exact pathway for other substrates different from fat [14,41] or carbohydrate-rich wastes. Sour cabbage contents already some proteins [42] on the level of agar plates [43]. The presence of hydrogen sulfide shows that proteins are decomposed in the DF also [44]. Therefore, biogas analysis requires checking gas content different from carbon dioxide, methane, hydrogen, and nitrogen [45]. One of the problems of the DF is the selection of material from waste to produce hydrogen [46]. The sour cabbage (cabbage preserved by lactic acid fermentation—in Middle—Europe—most common ensiling food example) is used as a substrate. The ensiling of sour cabbage (in cabbage is a natural process) results in 10% of a not successful production of sour cabbage and becomes a waste that needs to be utilized. Sour cabbage resulted in the highest hydrogen yield from some pH-reducing substrates. There was obtained immense volumes of methane in AD from kimchi (fermented Chinese cabbage) [47]. Kimchi was a part of kitchen waste [48] used for dark fermentation, but not separated, and could not be concluded on what range biogas came from kimchi. Chinese cabbage *Brassica rapa* subsp. *pekinensis* is a group of *Brassica rapa* from which sour cabbage is made. Another alluring case of sour cabbage is that during time volatile suspended solid changed. Sour cabbage also contains some salts [49], which can be enough for DF without adding salts [50] or nutrients [51]. Therefore, there was

relevant to check the feasibility of sour cabbage for hydrogen production. Another aim was testing the optimal pH and microaeration conditions of the process. Data of sour cabbage microaeration in acidic pH and raw inoculum for hydrogen production has not been reported [52]. Therefore, it seems to be worth digesting anaerobically sour cabbage of different VSS (different degrees of ensiling) checking if it is a potential hydrogen source as well as corn [53], rice [54], beets [55], and wheat [56]. Investigations of sour cabbage dark fermentation for 5 g VSS/L [28] and 10 g VSS/L [57], in neutral conditions, obtained promising results. Then experiments were continued for acidic pH values for 5 g VSS/L and 10 g VSS/L.

2. Materials and Methods

2.1. Description of Experiments

The outdated sour cabbage, unavailable as food, was taken from RENK Pomeranian Agri-food Wholesale Center S.A. The fermentation process of sour cabbage was performed in glass reactors of volume 2 L with a working volume (substrates with bacterial layer) of 1.2 L (Figure 1). Such reactors were successful for batch experiments, as proved by Dach et al. [58,59]. The experimental procedure is shown in Figure 2. The bacteria layer was a sludge from the biogas plant in Lubań (Pomerania). The inoculum used for experiments was coming from a mesophilic digester treating mainly maize silage and manure. They were kept in a water bath under mesophilic conditions (38 ± 2 °C). Before fermentation, the batch reactors (see Figure 2) were flushed with nitrogen to maintain strictly anaerobic conditions at the beginning of the process. The gas emitted by every fermenter was collected in a cylindrical vessel filled with a barrier liquid and water. Carbon dioxide dissolving in the water was eliminated by placing at the top the mixture by mass 1:10 detergents for dishes (Ludwik®, Warszawa, Poland) and diesel oil. Sour cabbage used for these experiments was three months fermented longer than sour cabbage used in [60]. The characteristics of substrates and the inoculum are shown in Table 1. The NREL norm [61] was applied for characteristics of inoculum and substrates.

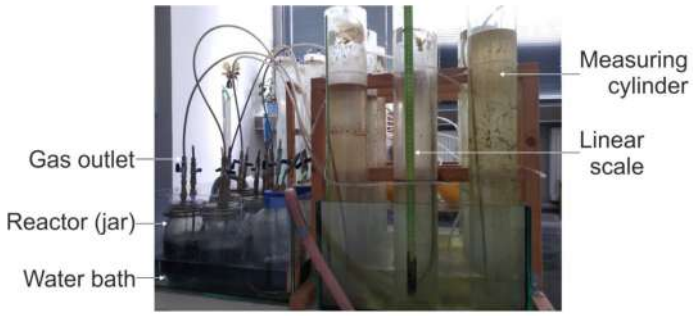

Figure 1. Photo of the experimental setup [60] [Reproduced with permission from Sołowski Heliyon Elsevier 2021].

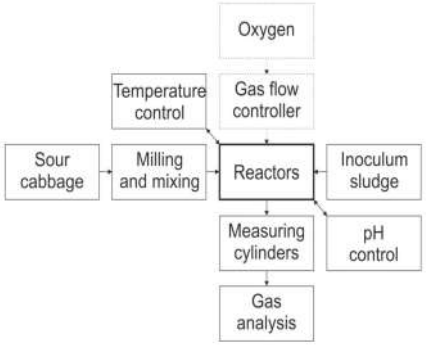

Figure 2. Sketch of the experimental procedure for biogas production by dark fermentation of sour cabbage [60] [Reproduced with permission from Sołowski Heliyon Elsevier 2021].

Table 1. The characteristics of inoculums and sour cabbage.

Material	pH	TS	VSS
Inoculum	8.24	1.31 ± 0.028%	29.11% TS ± 1.03%
Sour Cabbage	4.32	7.43 ± 0.02%	67.03% TS ± 1.02%

Either 5 g VSS/L or 10 g VSS/L volatile suspended solids (VSS) was applied to each batch of sour cabbage for the process. The substrate before the introduction to digestors was milled and mixed. In 5 g VSS/L of sour cabbage, after adding sour cabbage to inoculum, the pH value of the mixture was lowered (using 38% solution of HCl) from 7.9 to 6.0. The oxygen flow rates (OFR): 0, 0.58, 0.87 mL/h were applied for the substrate load 5 g VSS/L for sour cabbage as in [60]. OFR was increased gradually until hydrogen production disappeared. Thus, the last OFR checked was the limit value of hydrogen production at concentration 5 g VSS/L and pH 6.0. In the case of 10 g VSS/L, oxygen flow rates of 0 mL/h and 1.4 mL/h were tested for sour cabbage at pH 6.0 (also shifted with 38% HCl). Oxygen was added twice by syringe a day until the fermentation process stopped for 10 to 19 days, added during approximately 2 s. Microaeration had a pause beside the period from 3rd to 6th-day investigations. Batch experiments were finished when daily biogas production was below 1% of total biogas production.

2.2. Analytical Methods

The pH value was measured during days of a significant increase in biogas production, i.e., 1st–8th day, every seven days of the experiment, and the last day of the investigation. The pH after initial lowering was unchanged pH level, in the end, came back to the value before lowering at the final days of experiments. The biogas production was determined using the Owen method [62]. All of the experiments were carried out, in triplicate, in 12 reactors, the mean values for biogas measurements were reported. Collected biogases were sampled for measuring qualitative and quantitative parameters in one or two stages, exactly as in [44]. The device was calibrated twice a week. The second stage occurred if the hydrogen concentration of evaluated biogas exceeded 1000 ppm. Then a portion of gas (100 mL) was characterized using gas chromatography (GC) (Shimazu, Osaka, Japan) with a thermal conductivity detector (TCD) (Shimazu, Osaka, Japan). Argon—a gas carrier flew with a rate of 0.6 mL/h. GC-TCD (Shimazu, Osaka, Japan) was applied in silico packed single column Restek® of characteristics—2 m/2 mm ID 1/8″ OD Silica. GC–TCD allowed gas content determination of methane, hydrogen, carbon dioxide, nitrogen, oxygen, ethylene, and carbon monoxide. Added oxygen was later in results diminished in volumes of obtained biogas and assumed as ballast gases.

2.3. Methods of Elaborating

Volumes of measured biogas were normalized to standard conditions (0 °C and 1.013 bar) using Equation (7).

$$V_s = \frac{V_m \cdot T_s \cdot P_m}{T_m \cdot P_s} \quad (7)$$

where: V_s is a volume of measured gas at standard temperature and pressure, V_m is a volume of measured gas at ambient conditions, T_m is ambient temperature, T_s is a standard temperature, P_m is a ambient pressure and P_s is a standard pressure. Sulfur added with methionine as an additional source of hydrogen sulfide (supplied within sour cabbage) was determined according to [63], with Equation (8).

$$\text{Ratio} = \frac{94.11\ \%\ V_{H2S} \cdot \rho_{H2S}}{\text{Mass of sulphur added with sour cabbage}} \quad (8)$$

Hydrogen sulfide accumulated emission volume V_{H2S} multiplied by the density of hydrogen sulfide at room temperature ρ_{H2S} (1.313 g/cm^3), percentage of sulfur in hydrogen

sulfide (94.11%), and divided by the mass of sulfur added with sour cabbage gave the ratio (8).

3. Results and Analysis

The GC analysis determined the presence of methane, hydrogen, carbon dioxide, ethylene, and nitrogen concentrations. The gas analyzer also showed the presence of hydrogen sulfide. In the case of VSS 5 g/L, the pH value shortly after HCl addition was 6.0; then, subsequently 222.5 h (nine days) of fermentation, it drops to 5.0. After 453.4 h (11 days) of fermentation, the pH value returned to 7.5. The process was not as hydrogenotrophic like in Pradhan et al. [64]. During the process was observed hydrogen sulfide emission when hydrogen production occurred similar to [30].

3.1. Ethylene Production

In the case of low pH values (~6), ethylene generation was observed (see Figure 3). The production of ethylene was: 0.0015 L (for the oxygen flow rate 0.58 mL/h, VSS 5 g/L), 0.0023 L (for oxygen flow 0.87 mL/h, VSS 5 g/L) and 0.0016 L (for the OFR 1.4 mL/h, VSS 10 g/L). When ethylene production results from a process similar to OCM (oxidative coupling of methane) [65].

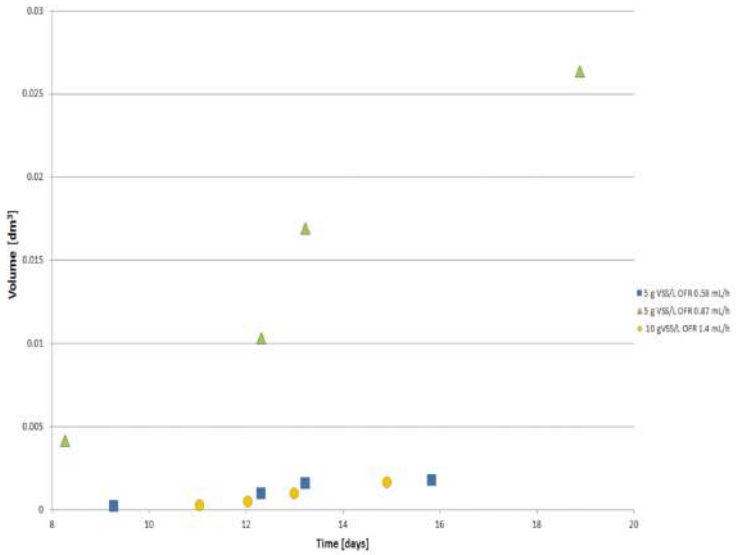

Figure 3. Time evolution of ethylene production during fermentation of sour cabbage with at different OFR and concentration.

The process OCM is a process working due to [66,67] like in reactions (9) and (10) (s subscript in reactions stands for surface).

$$[O]_S + CH_4 \rightarrow [OH]_s + CH_3 \quad (9)$$

$$2CH_3 \rightarrow C_2H_4 + H_2 \quad (10)$$

The ethylene concentration was at a constant level from the 9th to the 16th day. The ethylene was reported as a sign of the start of the ripening of fruit [68,69]. Then after checking sour cabbage of concentration 5 g VSS/L, there were provided results for 10 g VSS/L.

3.2. Methane and Hydrogen Production from Sour Cabbage

Under strict anaerobic conditions (see Figure 4, Table 2), the volume of methane and hydrogen produced during anaerobic conditions and pH 6.0 and microaeration. Methane and hydrogen productions at substrates concentrations 5 g VSS/L and 10 g VSS/L were

compared in Figure 4 (methane) and Figure 5 (hydrogen). They showed that the decrease of pH value to 6.0 results in decreased methane production (low pH value inhibited methane production by methanogenic bacteria). That was in agreement with [70]. However, a small addition of oxygen (to 0.58 mL/h) increased methane production. A further boost in oxygen flow rates (to 0.87 mL/h) decreased hydrogen production.

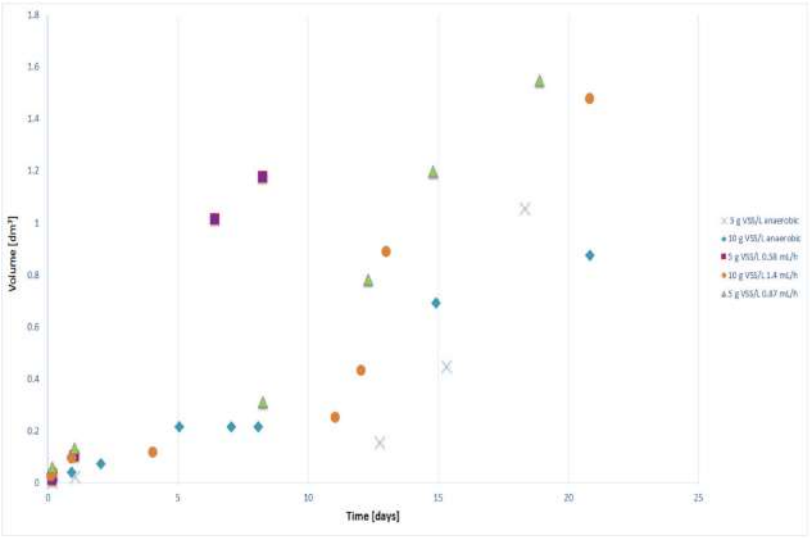

Figure 4. Time evolution of the total volume of methane for sour cabbage 5 g VSS/L and 10 g VSS/L at pH 6.0 and different OFR.

Table 2. Cumulative hydrogen and methane production in the different OFR.

Substrate	OFR [mL/h]	Cumulative Hydrogen [L]	Cumulative Methane [L]
Sour cabbage 5 g VSS/L	0	0.091	1.058
	0.58	0.107	0.73
	0.87	0.018	1.55
Sour cabbage 10 g VSS/L	0	0.081	1.47
	1.4	0.2	0.63

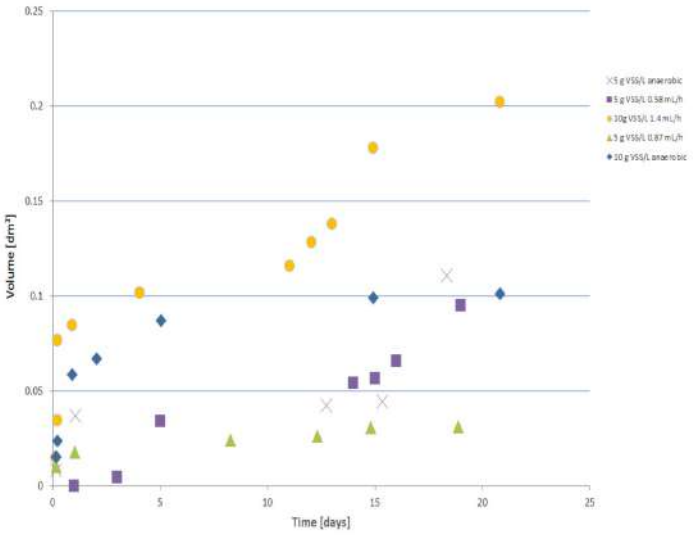

Figure 5. Time evolution of cumulative hydrogen production for sour cabbage (low VSS), 5 g VSS/L at pH 6.0 with different OFR and VSS.

The microaeration changed biogas volume and ratio of components in different VSS of sour cabbage. The oxygen was added twice a day for 22 days. A small oxygen addition OFR (0.58 mL/h) led to increment hydrogen production. A further increase in oxygen flow rate (0.87 mL/h) inhibited hydrogen production in comparison to OFR of 0 mL/h. Figure 5 showed the correlations of cumulative hydrogen production on various pH and VSS for sour cabbage of 5 g VSS/L. Fermentation length did not change on the influence of VSS only by pH change. The oxygen addition also in both VSS cases in different rates ranges from improved hydrogen production. In the case of sour cabbage, the positive related to anaerobic hydrogen production was the range of OFR from 0.58 mL/h to 0.87 mL/h for 5 g VSS/L. The range of OFR positive for hydrogen production (higher than strictly anaerobic) at pH 6.0 and 5 g VSS/L was much smaller than in the case of pH 7.5 [28,71]. The hydrogen yield in pH 6.0 was much higher than in pH 7.5, agreed with most hydrogenotrophic trends [20]. The addition of oxygen in low pH improved a slight yield analogically to neutral conditions [58]. OFR ranges narrow with a decrease of pH in the case of the sour cabbage. The hydrogen production in low pH was improved by microaeration for fresh sour cabbage [60] nearly 3% higher while for this sour cabbage almost 10% higher. Dark fermentation in low pH at 5 g VSS/L was from 5 to 50 times higher in the same VSS from neutral pH [58].

In Figure 4, at the most efficient hydrogen production case of DF from 5 g VSS/L of sour cabbage, hydrogen formed was gradually converted with carbon dioxide immediately in methane production there like in [72]. With higher hydrogen production was more carbon dioxide than in methane, thus, a concentration of it decreased with time. Oxygen and nitrogen were ballast gases not involved in biogas quality and quantity analysis [73]. Overall oxygen percentages in reactors were carried at ranges from 2% to 8% measured in received gas from cylinders. Added oxygen was later in result diminished in volumes of obtained biogas. Hydrogen production was higher than methane production on the second day of fermentation. After that day, methane production boosted even 40 times on the 18th day of fermentation. Sudden increment of methane responded to an increase of pH to 7.5 (from the 12th to the 19th day). Decrease of pH to a value of 6.0 increased hydrogen emission (from 4th to 11th day). This trend was induced by the formation of low organic acid in hydrogenotrophic digestion. The increase of pH to 7.5 was caused by surpassing the conversion of the acids into methane. A rise in pH by conversion of low organic acids was observed in [74]. Between the second and the eighth day, biogas was produced in volumes below amenable for measurement. After the nineth day of the experiment, biogas production returned for measurable volumes of biogas on the 19th day. Then biogas production stopped and was not observed at all. In the case of 10 g VSS/L, it can be discerned the difference of 1 mL of hydrogen between neutral pH [57] and strictly anaerobic at pH 6.0 (19 mL of hydrogen) from sour cabbage [60] (high VSS) (see Figure 5). Higher concentration led to longer hydrogen production, besides acidic pH that shortened fermentation time to 15 or 17 days.

3.3. Total Hydrogen Production vs. Total Hydrogen Sulphite Production and General Discussion

Ratios of cumulative hydrogen production vs. hydrogen sulfide emission on the sour cabbage fluctuated more than in [44]. In every investigated example, there is a sudden outburst of hydrogen production on the first day, then replaced with higher hydrogen sulfide production, more than from glycol ethylene digestion. The hydrogen sulfide outcome was also from bacterial rests as sour cabbage containing only from 3.4 to 6.8 mg/L of overall protein according to [63], then rests are a major source of protein. Some hydrogen sulfide occurred due to the digestion of methionine; however, this was only a small part of the emitted gas (see Figure 6 and Table 3).

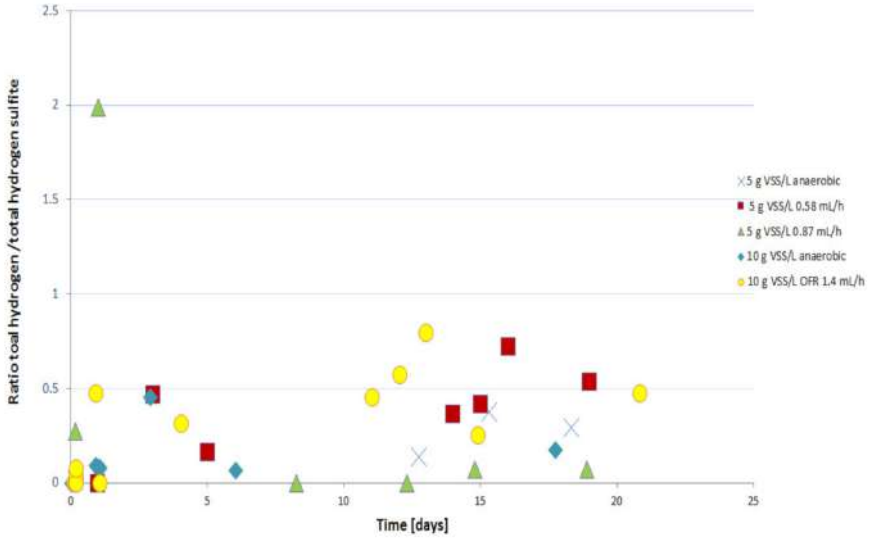

Figure 6. Time evolution ratio of cumulative hydrogen production vs. hydrogen sulfide emission for different concentrations and OFR.

Table 3. Sulphur added with sour cabbage in samples and the ratio sulfur ratio of sulfur converted in emitted hydrogen sulfide%.

Mass of Sour Cabbage Added [g VSS/L]	Mass of Sulphur in Added Sour Cabbage [mg VSS/L]	The Ratio of Sulphur Converted in Emitted H_2S%	OFR [mL/h]
5	3.4	130.8	0.58
5	3.4	40.8	0.87
5	3.4	5.46	0
10	6.8	70.6	1.4
10	6.8	26.9	0

The reaction of decomposition of protein (general formula of protein) by fermentation due to determined gas component analysis occurs like in Equation (11):

$$C_{400}H_{620}N_{100}O_{120}PS \rightarrow H_2 + CH_4 + CO_2 + C_2H_4 + CH_3OOH + C_2H_5COOH + H_2S \quad (11)$$

Microaeration for some ranges improves hydrogen production like for cotton. Hydrogen sulfide simultaneously increases but then with OFR raise, it is removed that agrees with [75].

On the OFR analysis, there can be observed that the fermentation of sour cabbage hydrogen production is more sensitive than methane production. This showed that in the case of high VSS [76], there were some ranges improving methane production yield that agreed with comparisons of Nguyen et al. [25] (fixing metabolism in the anaerobic digestion of lignocellulose) and Krayzelova et al. [77] (reduction of hydrogen sulfide). It can be discerned that after the 11th day (265 h) and 10 g VSS/L a significant growth of hydrogen production was observed—see Figure 5, due to pH decrease. Trends in the case of 5 g VSS/L loads were similar but occurred three days earlier. This pH decreased results from the production of short organic acids (butyric, acetic, and lactic). However, after 14th (load 5 g VSS/L) and 15th day (10 g VSS/L), the pH returned to the level of 7.5—the acids were consumed for methane production. The obtained hydrogen percentage in biogas reached 11.19% for 0.58 mL/h (1st day) for 5 g VSS/L and 22% for 10 g VSS/L at 1.4 mL/h (at 0.7-0.9th day of the process). In the first days, increments of hydrogen production were noticed most significantly, as in cotton [78] or fruit wastes [79]. Thus, it did not seem sensible to repeat for lower concentration. This was caused by a higher pH blocking acetogenesis and methane conversion [80]. The highest methane result for sour

cabbage was slightly higher than in acidic pH, with nonzero OFR for sour cabbage [60]. It showed a remarkable influence on the VSS level on methane production. In the case of VSS of 67%, there was not as much matter for digestion as in the VSS 89%. In the VSS 89% [49], sour cabbage was enough digested—anaerobic digestion bacteria easier convert it into methane.

The increase of concentration of sour cabbage to 10 g VSS/L with some microaeration OFR resulted in higher hydrogen production than in the case of strictly anaerobic. An increment of hydrogen production in the case of shifting pH [57] lowered the time of digestion. Biogas production in 10 g VSS/L and pH of 6.0 was shorter by two days, see Figure 5.

VSS 89% of sour cabbage [60] allowed producing hydrogen more efficiently than in the case of VSS 66.7%. VSS 89% occurred when the ensiling of sour cabbage just started appearing. The longest and with the highest efficiency was hydrogen production at acidic conditions that agreed with most results [81]. Different VSS of sour cabbage caused a more significant shift of biogas production in neutral than in acidic pH. For pH 6.0, the differences between substrates of various VSS with better hydrogen production results were for sour cabbage, while for pH 7.5, there was almost 28 times more methane [57]. Therefore, the shift of pH (see Figures 4 and 5) shrank differences of biogas volume due to VSS [49]. For pH 6.0, hydrogen production was 0.18 L for sour cabbage for 5 g VSS/L and 0.21 for 10 g VSS/L. The increase of OFR negatively influenced methane production from sour cabbage. The substrate increase resulted in higher hydrogen production, contrary to the glucose results of Pan et al. [82]. Higher substrate concentration led to longer hydrogen production. However, in the case of low pH, elongated to four days more, while in the case of neutral pH, to 10 days more [58]. An increase in substrate concentration augmented also the difference caused by VSS change.

In the case of raw (non-pretreated) inoculum, replacing hydrogen production with methane production was spontaneous. The difference between hydrogen productions from sour cabbage can be resulted in a saturation level of substrate for bacteria to produce hydrogen. Characteristics and investigations showed that sour cabbage possessed the optimal value for DF much higher than was at raw cabbage. Raw cabbage is the '0' step of the ensiling of cabbage [76]. Therefore, the substrate availability for methane or hydrogen production depends not only on pH but also on relevant dependent is not too high total solid parameter.

In the case of 10 g VSS/L and OFR 1.4 mL/h (see Figure 5), the biogas production length was 22 days and three days longer than from 5 g VSS/L. Hydrogen production up to the 4th day was higher than methane production. A longer inhibition of methane production caused an increase in the concentration of hydrogen. The concentration of 10 g VSS/L was not for the sour cabbage, shock load point observed by Kaparaju et al. [83] in wheat straw. Microaeration shortened hydrogen production increasing overall hydrogen yield, therefore converting substrate to hydrogen. The VSS difference changes yields of dark fermentation without influence on time fermentation. The most preferable for sour cabbage anaerobic digestion from the investigated value of VSS is VSS 89%.

Hydrogen production was significantly higher from sour cabbage than from key –lime and raw cabbage [76] but remarkably lower than cassava [84]. That was the outcome of using only the substrate without additional nutrients like agar plates [51] or special salts [85]. The results of untreated inoculum should feedback if treatment is worth like in cotton wastes. Thus, promising results showed that it could be an applicable additive for substrates that digestion increased pH like proteins [86]. The pH change can work as stress but in the case of sour cabbage worse than for bagasse, where it shifted process to hydrogen production by DF [21]. Due to high methane and hydrogen production, the presented process can be classified as dark fermentation or hydrogenotrophic anaerobic digestion.

4. Conclusions

Sour cabbage is a potential source for hydrogen production by dark fermentation either under strictly anaerobic conditions or with a small addition of oxygen, which inhibits methanogenesis and improves hydrogenesis. It was found that in the case of sour cabbage load 5 g VSS/L and initial pH 6.0, the highest hydrogen production was observed for flow rate 0.58 mL/h (hydrogen concentration reached up 12.2% in biogas). For an oxygen flow rate of 0.58 mL/h, the hydrogen production was slightly (15%) higher than strictly anaerobic conditions. The flow rate that can improve hydrogen production for a concentration of 5 g VSS/L feed rate must be higher than 0.53 mL/h and lower than 0.87 mL/h. The maximum methane production was reached under strictly anaerobic conditions. As the oxygen flow rates increased, methane production declined. Another relevant factor, more than the pH of a substrate, was a volatile suspended solids index that affects more than the factors mentioned earlier. Sour cabbage can produce quite a high efficiency of biogas without the addition of nutrients or salts thus is slightly cheaper for processing from most already checked substrates.

For 5 g VSS/L and oxygen flow rate 0.58 mL/h; 0.021 L of hydrogen and 0.06 L of methane were produced per gram of VSS. In the case of 10 g VSS/L and oxygen flow rate 1.4 mL/h 0.03 L of hydrogen and 0.14 L of methane were generated per gram of VSS. The percentage of hydrogen in biogas in 10 g VSS/L was up to 22%. Oxygen seems to play the role of a stress factor for bacteria. Proper control of dark fermentation or hydrogenotrophic anaerobic digestion using microaeration can be a tool in the stabilization of hydrogen production. In microaeration conditions, besides hydrogen, there can also obtain ethylene which is a raw chemical in polymer chemistry. The phenomena need further research.

Funding: The research was supported by the National Centre for Research and Development in Poland, under project no. BIOSTRATEG 3/344128/12/NCBR/2017, and Institute of Fluid-Flow Machinery, Polish Academy of Science in Gdansk (grant number FBW-44—Solowski).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data are included at manuscript.

Acknowledgments: Special thanks to Dariusz Czylkowski and Bartosz Hrycak for their help in GC analysis. Special thanks to RENK Pomeranian Agri-food Wholesale Center S.A for the possibility of using their wastes of sour cabbage that allowed performing this research.

Conflicts of Interest: The Author declare no conflict of interests.

References

1. Chaganti, S.R.; Kim, D.H.; Lalman, J.A. Dark fermentative hydrogen production by mixed anaerobic cultures: Effect of inoculum treatment methods on hydrogen yield. *Renew. Energy* **2012**, *48*, 117–121. [CrossRef]
2. Lovato, G.; Augusto, I.M.G.; Ferraz Júnior, A.D.N.; Albanez, R.; Ratusznei, S.M.; Etchebehere, C.; Zaiat, M.; Rodrigues, J.A.D. Reactor start-up strategy as key for high and stable hydrogen production from cheese whey thermophilic dark fermentation. *Int. J. Hydrog. Energy* **2021**, *46*, 27364–27379. [CrossRef]
3. Ochoa, C.; Hernández, M.A.; Bayona, O.L.; Cabeza, I.O.; Candela, A.M. Value—Added By—Products during Dark Fermentation of Agro—Industrial Residual Biomass: Metabolic Pathway Analysis. *Waste Biomass Valorization* **2021**, *12*, 5937–5948. [CrossRef]
4. Bustamante, M.A.; Nogués, I.; Jones, S.; Allison, G.G. The effect of anaerobic digestate derived composts on the metabolite composition and thermal behaviour of rosemary. *Sci. Rep.* **2019**, *9*, 1–15. [CrossRef] [PubMed]
5. Li, C.; Zhu, X.; Angelidaki, I. Carbon monoxide conversion and syngas biomethanation mediated by different microbial consortia. *Bioresour. Technol.* **2020**, *314*, 123739. [CrossRef] [PubMed]
6. Kumari, D.; Singh, R. Pretreatment of lignocellulosic wastes for biofuel production: A critical review. *Renew. Sustain. Energy Rev.* **2018**, *90*, 877–891. [CrossRef]
7. Detman, A.; Mielecki, D.; Chojnacka, A.; Salamon, A.; Błaszczyk, M.K.; Sikora, A. Cell factories converting lactate and acetate to butyrate: Clostridium butyricum and microbial communities from dark fermentation bioreactors. *Microb. Cell Fact.* **2019**, *18*, 1–12. [CrossRef] [PubMed]
8. Sharma, K. Carbohydrate-to-hydrogen production technologies: A mini-review. *Renew. Sustain. Energy Rev.* **2019**, *105*, 138–143. [CrossRef]

9. Dessì, P.; Lakaniemi, A.M.; Lens, P.N.L. Biohydrogen production from xylose by fresh and digested activated sludge at 37, 55 and 70 °C. *Water Res.* **2017**, *115*, 120–129. [CrossRef]
10. Lakaniemi, A.M.; Koskinen, P.E.P.; Nevatalo, L.M.; Kaksonen, A.H.; Puhakka, J.A. Biogenic hydrogen and methane production from reed canary grass. *Biomass Bioenergy* **2011**, *35*, 773–780. [CrossRef]
11. Detman, A.; Mielecki, D.; Pleśniak, Ł.; Bucha, M.; Janiga, M.; Matyasik, I.; Chojnacka, A.; Jędrysek, M.O.; Błaszczyk, M.K.; Sikora, A. Methane-yielding microbial communities processing lactate-rich substrates: A piece of the anaerobic digestion puzzle. *Biotechnol. Biofuels* **2018**, *11*, 1–18. [CrossRef] [PubMed]
12. Lu, L.; Ren, N.Q.; Zhao, X.; Wang, H.A.; Wu, D.; Xing, D.F. Hydrogen production, methanogen inhibition and microbial community structures in psychrophilic single-chamber microbial electrolysis cells. *Energy Environ. Sci.* **2011**, *4*, 1329–1336. [CrossRef]
13. Kotay, S.M.; Das, D. Novel dark fermentation involving bioaugmentation with constructed bacterial consortium for enhanced biohydrogen production from pretreated sewage sludge. *Int. J. Hydrogen Energy* **2009**, *34*, 7489–7496. [CrossRef]
14. Pachapur, V.L.; Kutty, P.; Pachapur, P.; Brar, S.K.; Le Bihan, Y.; Galvez-Cloutier, R.; Buelna, G. Seed pretreatment for increased hydrogen production using mixed-culture systems with advantages over pure-culture systems. *Energies* **2019**, *12*, 1–26. [CrossRef]
15. Li, Q.; Guo, C.; Liu, C.Z. Dynamic microwave-assisted alkali pretreatment of cornstalk to enhance hydrogen production via co-culture fermentation of Clostridium thermocellum and Clostridium thermosaccharolyticum. *Biomass Bioenergy* **2014**, *64*, 220–229. [CrossRef]
16. Perez-Pimienta, J.A.; Flores-Gómez, C.A.; Ruiz, H.A.; Sathitsuksanoh, N.; Balan, V.; da Costa Sousa, L.; Dale, B.E.; Singh, S.; Simmons, B.A. Evaluation of agave bagasse recalcitrance using AFEX^{TM}, autohydrolysis, and ionic liquid pretreatments. *Bioresour. Technol.* **2016**, *211*, 216–223. [CrossRef] [PubMed]
17. Van Schoubroeck, S.; Van Dael, M.; Van Passel, S.; Malina, R. A review of sustainability indicators for biobased chemicals. *Renew. Sustain. Energy Rev.* **2018**, *94*, 115–126. [CrossRef]
18. Muñoz-Páez, K.M.; Alvarado-Michi, E.L.; Buitrón, G.; Valdez-Vazquez, I. Distinct effects of furfural, hydroxymethylfurfural and its mixtures on dark fermentation hydrogen production and microbial structure of a mixed culture. *Int. J. Hydrogen Energy* **2019**, *44*, 2289–2297. [CrossRef]
19. Li, Y.; Zhang, Q.; Deng, L.; Liu, Z.; Jiang, H.; Wang, F. Biohydrogen production from fermentation of cotton stalk hydrolysate by Klebsiella sp. WL1316 newly isolated from wild carp (*Cyprinus carpio* L.) of the Tarim River basin. *Appl. Microbiol. Biotechnol.* **2018**, *102*, 4231–4242. [CrossRef] [PubMed]
20. Karaosmanoglu Gorgeç, F.; Karapinar, I. Production of biohydrogen from waste wheat in continuously operated UPBR: The effect of influent substrate concentration. *Int. J. Hydrogen Energy* **2019**, *44*, 17323–17333. [CrossRef]
21. Mechery, J.; Thomas, D.M.; Kumar, C.S.P.; Joseph, L.; Sylas, V.P. Biohydrogen production from acidic and alkaline hydrolysates of paddy straw using locally isolated facultative bacteria through dark fermentation. *Biomass Convers. Biorefinery* **2019**, *11*, 1263–1272. [CrossRef]
22. Chi, C.H.; Chen, K.W.; Huang, J.J.; Chuang, Y.C.; Wu, M.H. Gas composition in Clostridium septicum gas gangrene. *J. Formos. Med. Assoc.* **1995**, *94*, 757–759.
23. Camargo, F.P.; Sakamoto, I.K.; Bize, A.; Duarte, I.C.S.; Silva, E.L.; Varesche, M.B.A. Screening design of nutritional and physico-chemical parameters on bio-hydrogen and volatile fatty acids production from Citrus Peel Waste in batch reactors. *Int. J. Hydrog. Energy* **2020**, *46*, 7794–7809. [CrossRef]
24. Sołowski, G.; Konkol, I.; Cenian, A. Production of hydrogen and methane from lignocellulose waste by fermentation. A review of chemical pretreatment for enhancing the efficiency of the digestion process. *J. Clean. Prod.* **2020**, *267*, 121721. [CrossRef]
25. Nguyen, D.; Khanal, S.K. A little breath of fresh air into an anaerobic system: How microaeration facilitates anaerobic digestion process. *Biotechnol. Adv.* **2018**, *36*, 1971–1983. [CrossRef] [PubMed]
26. Krayzelova, L.; Bartacek, J.; Díaz, I.; Jeison, D.; Volcke, E.I.P.; Jenicek, P. Microaeration for hydrogen sulfide removal during anaerobic treatment: A review. *Rev. Environ. Sci. Biotechnol.* **2015**, *14*, 703–725. [CrossRef]
27. Wysocka, I.; Gębicki, J.; Namieśnik, J. Technologies for deodorization of malodorous gases. *Environ. Sci. Pollut. Res.* **2019**, *26*, 9409–9434. [CrossRef]
28. Sołowski, G.; Hrycak, B.; Czylkowski, D.; Konkol, I.; Pastuszak, K.; Cenian, A. Hydrogen and Methane Production Under Conditions of Dark Fermentation Process with Low Oxygen Concentration. In *Re-Use and Recycling of Materials Solid Waste Management and Water Treatment*; Jibin, K., Kalarikkal, N., Thomas, S., Nzihou, A., Eds.; River Publisher: Gistrup, Denmark, 2019; pp. 263–272. ISBN 9788770220583.
29. Khoshnevisan, B.; Tsapekos, P.; Alfaro, N.; Díaz, I.; Fdz-Polanco, M.; Rafiee, S.; Angelidaki, I. A review on prospects and challenges of biological H2S removal from biogas with focus on biotrickling filtration and microaerobic desulfurization. *Biofuel Res. J.* **2017**, *4*, 741–750. [CrossRef]
30. Sołowski, G.; Konkol, I.; Cenian, A. Methane and Hydrogen Production from Cotton Wastes in Dark Fermentation Process Under Anaerobic and Microaerobic Conditions. In *Frontiers in Water-Energy-Nexus—Nature-Based Solutions, Advanced Technologies and Best Practices for Environmental Sustainability*; Naddeo, V., Balakrishnan, M., Choo, K.-H., Eds.; Springer: Cham, Switzerland, 2020; pp. 285–287. ISBN 978-3-030-13067-1.
31. Abo-Hashesh, M.; Hallenbeck, P.C. Microaerobic dark fermentative hydrogen production by the photosynthetic bacterium, Rhodobacter capsulatus JP91. *Int. J. Low-Carbon Technol.* **2012**, *7*, 97–103. [CrossRef]

32. Hallenbeck, P.C.; Abo-Hashesh, M.; Ghosh, D. Strategies for improving biological hydrogen production. *Bioresour. Technol.* **2012**, *110*, 1–9. [CrossRef]
33. Bartacek, J.; Zabranska, J.; Lens, P.N.L. Developments and constraints in fermentative hydrogen production. *Biofuels Bioprod. Biorefining* **2007**, *1*, 201–214. [CrossRef]
34. Hussy, I.; Hawkes, F.R.; Dinsdale, R.; Hawkes, D.L. Continuous fermentative hydrogen production from sucrose and sugarbeet. *Int. J. Hydrog. Energy* **2005**, *30*, 471–483. [CrossRef]
35. Woodward, J.; Orr, M.; Cordray, K.; Greenbaum, E. Enzymatic production of biohydrogen. *Nature* **2000**, *405*, 1014–1015. [CrossRef]
36. Pradhan, N.; Dipasquale, L.; d'Ippolito, G.; Fontana, A.; Panico, A.; Lens, P.N.L.; Pirozzi, F.; Esposito, G. Kinetic modeling of fermentative hydrogen production by Thermotoga neapolitana. *Int. J. Hydrog. Energy* **2016**, *41*, 4931–4940. [CrossRef]
37. Hawkes, F.R.; Hussy, I.; Kyazze, G.; Dinsdale, R.; Hawkes, D.L. Continuous dark fermentative hydrogen production by mesophilic microflora: Principles and progress. *Int. J. Hydrog. Energy* **2007**, *32*, 172–184. [CrossRef]
38. Skorek, J.; Cebula, J.; Latocha, L.; Kalina, J. Pozyskiwanie i energetyczne wykorzystanie biogazu z biogazowni rolniczych. *Gospod. Paliwami Energ.* **2003**, *12*, 15–19.
39. D'Ippolito, G.; Squadrito, G.; Tucci, M.; Esercizio, N.; Sardo, A.; Vastano, M.; Lanzilli, M.; Fontana, A.; Cristiani, P. Electrostimulation of hyperthermophile Thermotoga neapolitana cultures. *Bioresour. Technol.* **2021**, *319*, 124078. [CrossRef] [PubMed]
40. Lian, T.; Zhang, W.; Cao, Q.; Wang, S.; Yin, F.; Chen, Y.; Zhou, T.; Dong, H. Optimization of lactate production from co-fermentation of swine manure with apple waste and dynamics of microbial communities. *Bioresour. Technol.* **2021**, *336*, 125307. [CrossRef]
41. García, A.B.; Cammarota, M.C. Biohydrogen production from pretreated sludge and synthetic and real biodiesel wastewater by dark fermentation. *Int. J. Energy Res.* **2019**, *43*, 1586–1596. [CrossRef]
42. Bhatia, S.K.; Jagtap, S.S.; Bedekar, A.A.; Bhatia, R.K.; Rajendran, K.; Pugazhendhi, A.; Rao, C.V.; Atabani, A.E.; Kumar, G.; Yang, Y.H. Renewable biohydrogen production from lignocellulosic biomass using fermentation and integration of systems with other energy generation technologies. *Sci. Total Environ.* **2021**, *765*, 144429. [CrossRef] [PubMed]
43. Pan, C.M.; Fan, Y.T.; Xing, Y.; Hou, H.W.; Zhang, M.L. Statistical optimization of process parameters on biohydrogen production from glucose by *Clostridium* sp. Fanp2. *Bioresour. Technol.* **2008**, *99*, 3146–3154. [CrossRef] [PubMed]
44. Sołowski, G.; Ziminski, T.; Cenian, A. A shift from anaerobic digestion to dark fermentation in glycol ethylene fermentation. *Environ. Sci. Pollut. Res.* **2021**, *28*, 15556–15564. [CrossRef] [PubMed]
45. Rangel, C.; Sastoque, J.; Calderon, J.; Mosquera, J.; Velasquez, P.; Cabezab, I.; Acevedob, P. Hydrogen production by dark fermentation process: Effect of initial organic load. *Chem. Eng. Trans.* **2020**, *79*, 133–138. [CrossRef]
46. Stanislaus, M.S.; Zhang, N.; Yuan, Y.; Zheng, H.; Zhao, C.; Hu, X.; Zhu, Q.; Yang, Y. Improvement of biohydrogen production by optimization of pretreatment method and substrate to inoculum ratio from microalgal biomass and digested sludge. *Renew. Energy* **2018**, *127*, 670–677. [CrossRef]
47. Kafle, G.K.; Kim, S.H.; Sung, K.I. Batch anaerobic co-digestion of Kimchi factory waste silage and swine manure under mesophilic conditions. *Bioresour. Technol.* **2012**, *124*, 489–494. [CrossRef] [PubMed]
48. Jo, J.H.; Jeon, C.O.; Lee, D.S.; Park, J.M. Process stability and microbial community structure in anaerobic hydrogen-producing microflora from food waste containing kimchi. *J. Biotechnol.* **2007**, *131*, 300–308. [CrossRef] [PubMed]
49. Petäjä, E.; Mylleniemi, P.; Petäjä, P. Use of inoculated lactic acid bacteria in fermenting sour cabbage. *Agric. Food Sci.* **2008**, *9*, 37–48. [CrossRef]
50. Nath, K.; Kumar, A.; Das, D. Effect of some environmental parameters on fermentative hydrogen production by Enterobacter cloacae DM11. *Can. J. Microbiol.* **2006**, *52*, 525–532. [CrossRef] [PubMed]
51. Asada, Y.; Tokumoto, M.; Aihara, Y.; Oku, M.; Ishimi, K.; Wakayama, T.; Miyake, J.; Tomiyama, M.; Kohno, H. Hydrogen production by co-cultures of Lactobacillus and a photosynthetic bacterium, Rhodobacter sphaeroides RV. *Int. J. Hydrogen Energy* **2006**, *31*, 1509–1513. [CrossRef]
52. Mishra, P.; Krishnan, S.; Rana, S.; Singh, L.; Sakinah, M.; Ab Wahid, Z. Outlook of fermentative hydrogen production techniques: An overview of dark, photo and integrated dark-photo fermentative approach to biomass. *Energy Strateg. Rev.* **2019**, *24*, 27–37. [CrossRef]
53. Bundhoo, Z.M.A. Potential of bio-hydrogen production from dark fermentation of crop residues: A review. *Int. J. Hydrogen Energy* **2019**, *44*, 17346–17362. [CrossRef]
54. Zhang, L.; Li, Y.; Liu, X.; Ren, N.; Ding, J. Lignocellulosic hydrogen production using dark fermentation by *Clostridium lentocellum* strain Cel10 newly isolated from *Ailuropoda melanoleuca* excrement. *RSC Adv.* **2019**, *9*, 11179–11185. [CrossRef]
55. Panagiotopoulos, I.A.; Bakker, R.R.; Budde, M.A.W.; de Vrije, T.; Claassen, P.A.M.; Koukios, E.G. Fermentative hydrogen production from pretreated biomass: A comparative study. *Bioresour. Technol.* **2009**, *100*, 6331–6338. [CrossRef] [PubMed]
56. Özmihci, S.; Kargi, F. Dark fermentative bio-hydrogen production from waste wheat starch using co-culture with periodic feeding: Effects of substrate loading rate. *Int. J. Hydrogen Energy* **2011**, *36*, 7089–7093. [CrossRef]
57. Sołowski, G.; Hrycak, B.; Czylkowski, D.; Pastuszak, K.; Cenian, A. Oxygen sensitivity of hydrogenesis' and methanogenesis'. In *Contemporary Problems of Power Engineering and Environmental Protection 2017*; Pikoń, K., Lucyna, C., Eds.; Department of Technologies and Installations for Waste Management Copyright: Gliwice, Poland, 2018; pp. 157–159. ISBN 978-83-950087-1-9.
58. Marks, S.; Dach, J.; Garcia-Morales, J.L.; Fernandez-Morales, F.J. Bio-energy generation from synthetic winery wastewaters. *Appl. Sci.* **2020**, *10*, 1–9. [CrossRef]

59. Janczak, D.; Malinska, K.; Czekała, W.; Cáceres, R.; Lewicki, A.; Dach, J. Biochar to reduce ammonia emissions in gaseous and liquid phase during composting of poultry manure with wheat straw. *Waste Manag.* **2017**, *66*, 36–45. [CrossRef] [PubMed]
60. Sołowski, G.; Pastuszak, K. Modelling of dark fermentation of glucose and sour cabbage. *Heliyon* **2021**, *7*, e07690. [CrossRef] [PubMed]
61. Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, A.; Sluiter, J.; Templeton, D. *Preparation of Samples for Compositional Analysis: Laboratory Analytical Procedure (LAP)*; National Renewable Energy Laboratory: Golden, CO, USA, 2008.
62. Logan, B.E.; Oh, S.E.; Kim, I.S.; Van Ginkel, S. Biological hydrogen production measured in batch anaerobic respirometers. *Environ. Sci. Technol.* **2002**, *36*, 2530–2535. [CrossRef] [PubMed]
63. Jagannath, A.; Raju, P.S.; Bawa, A. A Two-Step Controlled Lactic Fermentation of Cabbage for Improved Chemical and Microbiological Qualities *. *J. Food Qual.* **2012**, *35*, 13–20. [CrossRef]
64. Pradhan, N.; d'Ippolito, G.; Dipasquale, L.; Esposito, G.; Panico, A.; Lens, P.N.L.; Fontana, A. Simultaneous synthesis of lactic acid and hydrogen from sugars via capnophilic lactic fermentation by Thermotoga neapolitana cf capnolactica. *Biomass Bioenergy* **2019**, *125*, 17–22. [CrossRef]
65. Stansch, Z.; Mleczko, L.; Baerns, M. Comprehensive Kinetics of Oxidative Coupling of Methane over the La_2O_3 /CaO Catalyst. *Ind. Eng. Chem. Res.* **1997**, *36*, 2568–2579. [CrossRef]
66. Lomonosov, V.I.; Sinev, M.Y. Oxidative coupling of methane: Mechanism and kinetics. *Kinet. Catal.* **2016**, *57*, 647–676. [CrossRef]
67. Ortiz-Bravo, C.A.; Figueroa, S.J.A.; Portela, R.; Chagas, C.A.; Bañares, M.A.; Toniolo, F.S. Elucidating the structure of the W and Mn sites on the Mn-Na2WO4/SiO2 catalyst for the oxidative coupling of methane (OCM) at real reaction temperatures. *J. Catal.* **2021**. [CrossRef]
68. Theologis, A. One rotten apple spoils the whole bushel: The role of ethylene in fruit ripening. *Cell* **1992**, *70*, 181–184. [CrossRef]
69. Zaidi, N.A.; Tahir, M.W.; Vinayaka, P.P.; Lucklum, F.; Vellekoop, M.; Lang, W. Detection of Ethylene Using Gas Chromatographic System. *Procedia Eng.* **2016**, *168*, 380–383. [CrossRef]
70. Ferraro, A.; Massini, G.; Mazzurco Miritana, V.; Rosa, S.; Signorini, A.; Fabbricino, M. A novel enrichment approach for anaerobic digestion of lignocellulosic biomass: Process performance enhancement through an inoculum habitat selection. *Bioresour. Technol.* **2020**, *313*, 123703. [CrossRef] [PubMed]
71. Sołowski, G.; Konkol, I.; Cenian, A. Methane and hydrogen production from cotton waste by dark fermentation under anaerobic and micro-aerobic conditions. *Biomass Bioenergy* **2020**, *138*, 105576. [CrossRef]
72. Zhang, L.; Loh, K.-C.; Zhang, J. Enhanced biogas production from anaerobic digestion of solid organic wastes: Current status and prospects. *Bioresour. Technol. Rep.* **2018**, *5*, 280–296. [CrossRef]
73. Bartela, Ł.; Katla, D.; Skorek-Osikowska, A. Evaluation of conceptual electrolysis-based energy storage systems using gas expanders. *Int. J. Hydrog. Energy* **2021**, *46*, 20171–20182. [CrossRef]
74. Grosser, A.; Neczaj, E. Enhancement of biogas production from sewage sludge by addition of grease trap sludge. *Energy Convers. Manag.* **2016**, *125*, 301–308. [CrossRef]
75. Theuerl, S.; Klang, J.; Prochnow, A. Process disturbances in agricultural biogas production—Causes, mechanisms and effects on the biogas microbiome: A review. *Energies* **2019**, *12*, 365. [CrossRef]
76. Sołowski, G.; Konkol, I.; Hrycak, B.; Czylkowski, D. Hydrogen and Methane Production under Conditions of Anaerobic Digestion of Key-Lime and Cabbage Wastes. *Agritech* **2019**, *39*, 243–250. Available online: https://jurnal.ugm.ac.id/agritech/article/view/35848/25481 (accessed on 20 January 2021). [CrossRef]
77. Pokorna-Krayzelova, L.; Vejmelková, D.; Selan, L.; Jenicek, P.; Volcke, E.I.P.; Bartacek, J. Final products and kinetics of biochemical and chemical sulfide oxidation under microaerobic conditions. *Water Sci. Technol.* **2018**, *78*, 1916–1924. [CrossRef]
78. Sołowski, G.; Konkol, I.; Shalaby, M.; Cenian, A. Rapid hydrogen generation from cotton wastes by mean of dark fermentation. *SN Appl. Sci.* **2020**, *2*, 1438. [CrossRef]
79. Cieciura-Włoch, W.; Borowski, S.; Otlewska, A. Biohydrogen production from fruit and vegetable waste, sugar beet pulp and corn silage via dark fermentation. *Renew. Energy* **2020**, *153*, 1226–1237. [CrossRef]
80. Atasoy, M.; Cetecioglu, Z. Bio-augmentation of mixed culture fermentation by Clostridium butyricum to enhance butyric acid production. *Bioresour. Technol.* **2020**, *8*, 104496.
81. Venturin, B.; Frumi Camargo, A.; Scapini, T.; Mulinari, J.; Bonatto, C.; Bazoti, S.; Pereira Siqueira, D.; Maria Colla, L.; Alves, S.L.; Paulo Bender, J.; et al. Effect of pretreatments on corn stalk chemical properties for biogas production purposes. *Bioresour. Technol.* **2018**, *266*, 116–124. [CrossRef]
82. Pan, C.M.; Fan, Y.T.; Zhao, P.; Hou, H.W. Fermentative hydrogen production by the newly isolated Clostridium beijerinckii Fanp3. *Int. J. Hydrog. Energy* **2008**, *33*, 5383–5391. [CrossRef]
83. Kaparaju, P.; Serrano, M.; Thomsen, A.B.; Kongjan, P.; Angelidaki, I. Bioethanol, biohydrogen and biogas production from wheat straw in a biorefinery concept. *Bioresour. Technol.* **2009**, *100*, 2562–2568. [CrossRef]
84. Su, H.; Cheng, J.; Zhou, J.; Song, W.; Cen, K. Improving hydrogen production from cassava starch by combination of dark and photo fermentation. *Int. J. Hydrog. Energy* **2009**, *34*, 1780–1786. [CrossRef]
85. Mishra, P.; Thakur, S.; Mahapatra, D.M.; Wahid, Z.A.; Liu, H.; Singh, L. Impacts of nano-metal oxides on hydrogen production in anaerobic digestion of palm oil mill effluent—A novel approach. *Int. J. Hydrog. Energy* **2018**, *43*, 2666–2676. [CrossRef]
86. Tsapekos, P.; Kougias, P.G.; Angelidaki, I. Mechanical pretreatment for increased biogas production from lignocellulosic biomass; predicting the methane yield from structural plant components. *Waste Manag.* **2018**, *78*, 903–910. [CrossRef] [PubMed]