Article

ANALYSIS OF BIOGAS COMPONENT PRODUCTION DURING ANAEROBIC DIGESTION OF SOUR CABBAGE IN MICROAERATION CONDITIONS UNDER DIFFERENT pH CONDITIONS

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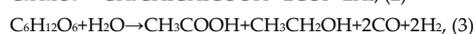
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Abstract In the article, were checked influences of microaeration, pH, and VSS (Volatile Suspended Solid) for sour cabbage anaerobic digestion. Results fermentation of sour cabbage under the condition of small oxygen addition are presented in this research can be classified as dark fermentation or hydrogenotrophic anaerobic digestion. The investigations were carried out for two concentrations 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. In cases of 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 is produced per gram of VSS. In this case, VSS 10 g/L and oxygen flow rate 1.4 mL/h at pH 6.0, 0.03 L of hydrogen is 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/L. Another relevant factor is the volatile suspended solid factor of sour cabbage that caused optimal hydrogen production at VSS 89.32%.

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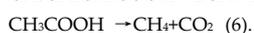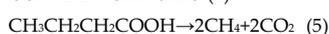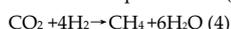
1. Introduction

Dark fermentation (DF) is a type 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 hydrolysed, 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 as 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]. Generally, in the DF process, bacterial sludge (inoculum) is pretreated by stressing 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 basic 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 be probably a stable supplemental method for other approaches to hydrogen production [24]. The next problem is a hydrogen sulphide 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 enhances hydrogen production [28] like anaerobic digestion enhanced methane production [29]. Thus, it seemed worth checking which process, methanogenesis or hydrogenesis, 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 in hydrogen production in photofermentation and was called microaerobic DF [27]. The process of DF proceeds along with one of three possible pathways [33,34]. Bartacek et al. [33] and Woodward et al. [35] pointed out three thermodynamically possible dark fermentation pathways 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 is the one with 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]

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

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

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

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 [42]. In sour cabbage, there is little proteins [57] on the level of agar plates [43]. The presence of hydrogen sulfide shows, that proteins are also decomposed [44]. Therefore, biogas analysis requires checking of presence of gas 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 that is preserved by lactic acid fermentation -in Middle – Europe –most common in food example of ensiling food) 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. Such a combination of sour cabbage microaeration in different 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 they 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 and not available as food were 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 2). Such reactors were successful for batch experiments as proved by Dach et al. [58,59]. A sketch of the experimental procedure for hydrogen production by DF of sour cabbage is shown in Figure 1. The bacteria layer was a sludge from the biogas plant in Lubań near Gdansk. 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 produced by every fermenter was collected in a cylindrical vessel filled with water and a barrier liquid. The water for eliminating carbon dioxide dissolving was on top marked with the mixture by mass 1:10 detergents for dishes (Ludwik ®) and diesel oil. Sour cabbage used for the experiments was 3 months longer fermented than sour cabbage used in [60]. The characteristics of the inoculum are shown in Table 1.

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 similar to [60]. OFR was gradually increased 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 (shifted also 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 continued until daily biogas production was less than 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 day 8th day, every 7 days of the experiment, and the last day of the investigation. The pH after initial lowering was unchanged thus pH level in the end came back to the value before lowering at last days of experiment. The biogas production was determined using the Owen method [61]. All of the experiments were carried out, in triplicate, in 12 reactors, the mean values for biogas measurements are reported. The qualitative and quantitative parameters of the collected biogases were determined in one or two stages exactly like in [44]. The calibration of the device was performed twice a week. The second stage occurred if the hydrogen concentration of evaluated biogas was above 1000 ppm. Then a portion of gas (100 mL) was characterized using gas chromatography (GC) with a thermal conductivity detector (TCD). Argon - a gas carrier flew with a rate of 0.6 mL/h. GC-TCD was applied in silico packed single column Restek® of characteristics - 2m/2mm ID 1/8'' OD Silica. GC –TCD allowed for the determination of hydrogen, methane nitrogen, oxygen, carbon dioxide, ethylene, and carbon monoxide. Added oxygen was later in results diminished in volumes of obtained biogas and assumed as ballast gases. The characteristics were made in agreement with to NREL norm [62]. The characteristics of the substrates were given in table 1.
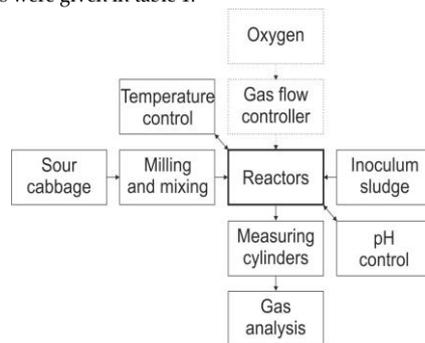

Figure 1 Sketch of the experimental procedure for hydrogen production by dark fermentation
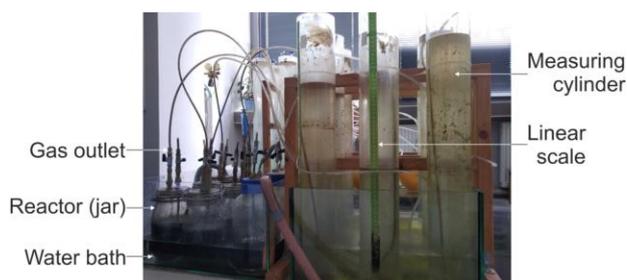
of sour cabbage.

Figure 2 Photo of the experimental setup.

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%

2.3.   Methods of elaborating.

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

$$V_s = \frac{V_m \cdot T_s \cdot P_m}{T_m \cdot P_s} \tag{7}$$

The volume presented in articles and concentration is made using equation 1.

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, and P_s is a standard pressure. Sulfur added with methionine as an additional source of hydrogen sulphide (supplied within sour cabbage) was calculated according to [63].

$$Ratio = \frac{94.11\,\% \; V_{H2S} \cdot \rho_{H2S}}{Mass\ of\ sulphur\ added\ with\ sour\ cabbage} \tag{8}$$

Hydrogen sulphide accumulated emission volume multiplied by the density of hydrogen sulphide at room temperature ρ_{H2S} (1.313 g/cm^3), percentage of sulphur in hydrogen sulphide (94.11%), and divided by the mass of sulphur added with sour cabbage gave the ratio (8).

3. Results and analysis

The GC analysis allowed the determination of methane, hydrogen, carbon dioxide, ethylene, and nitrogen concentrations. The gas analyzer also showed the presence of hydrogen sulphide. In the case of VSS 5g/L, the pH value shortly after HCl addition was 6.0; then after 222.5 h (9 days) of fermentation, it drops to 5.0. After 453.4 h (11 days) of fermentation, the pH value returned back to 7.5. The process was not so hydrogenotrophic like in Pradhan et al. [64].. During the process, was observed hydrogen sulphide emission when hydrogen production occurred similar to [30].

3.1. Ethylene production

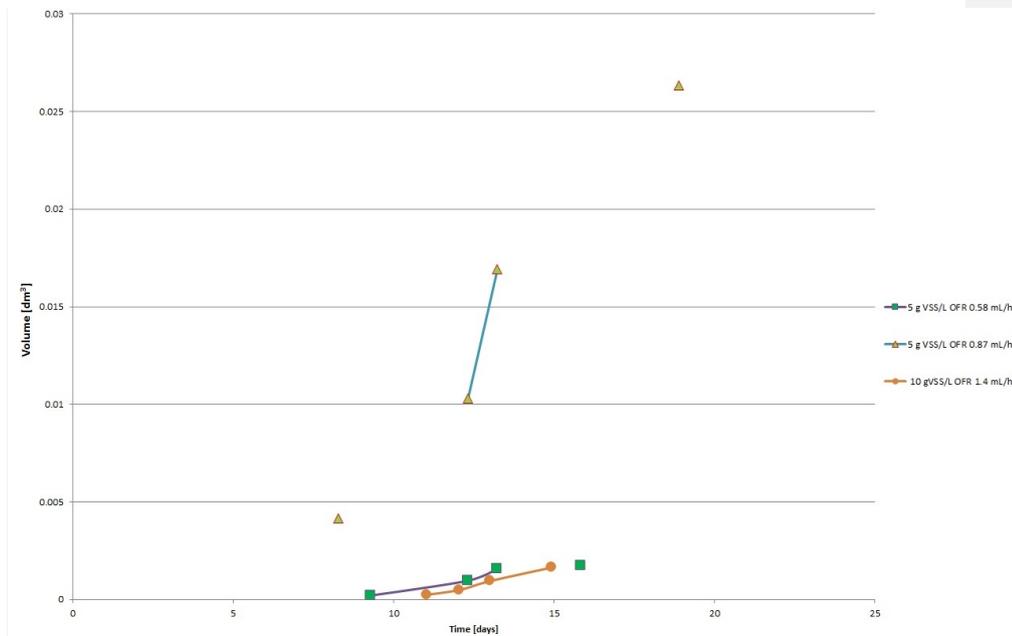> **Commented [KM1]:** Add from colcot a

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

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].

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

$$[O]_s + CH_4 \rightarrow [OH]_s + CH_3. \qquad (9)$$
$$2CH_3. \rightarrow C_2H_4 + H_2 \qquad (10)$$
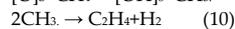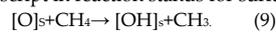
At the same time, production of an additional amount (up to 2% of hydrogen) of hydrogen for the oxygen flow rate of 0.87 mL/h or (up to 13%) in for the OFR 0.58 mL/h (see Figure 5). The ethylene concentration was at a constant level from the 9th to the 16th day. The ethylene was reported as a sign of 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 production from sour cabbage

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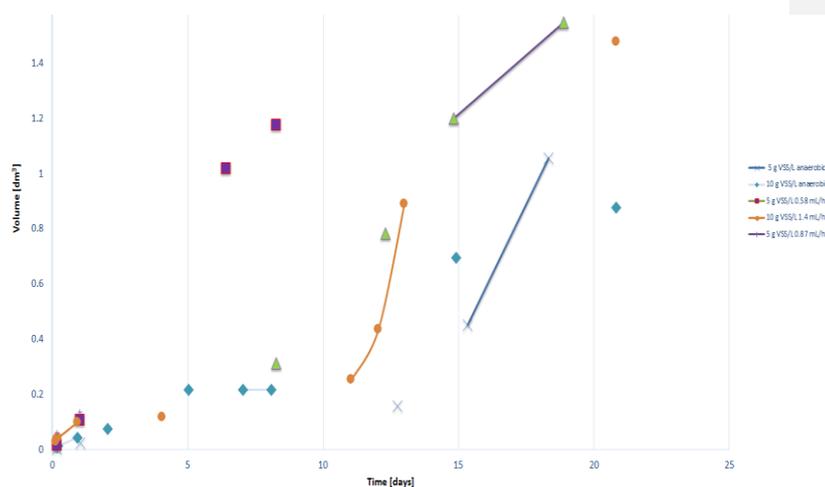
Figure 4 Time evolution of the total volume of methane for sour cabbage 5 g VSS/L and 10 g VSS/L

at pH 6.0 and different OFR.

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.

Table 2 Cumulative hydrogen and methane production in the different OFR

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

3.1. Total hydrogen production vs total hydrogen sulphite production and general discussion

The methane and hydrogen production at substrate load 5 g VSS/L and 10 g VSS/L for initial pH values 6.0 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.
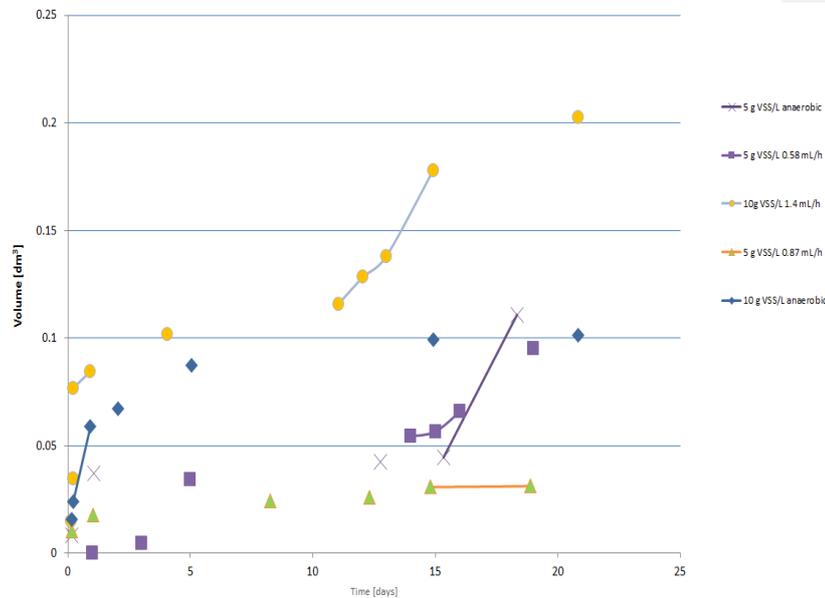
Figure 5. Time evolution of cumulative hydrogen production for sour cabbage (low VSS), 5 g VSS/L

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) can lead 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. From investigated parameters, the length of fermentation 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 in comparison 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 in analogy to neutral conditions. 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] just up to 3% higher while for this sour cabbage up to 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 for 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 concentration of it decreased with time. Oxygen and nitrogen are ballast gases that were not involved in biogas quality and quantity analysis [73]. Overall oxygen percentage in reactors was kept in the range 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 2nd day of fermentation. After that day, methane production boosted even 40 times on the 18th day of fermentation. It can be discerned, that a sudden increase of pH to 7.5 responded to increment of methane (from the 12th to the 19th day), while a decrease of pH to increase of hydrogen (from 4th to 11th day)-pH 6.0. This 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. Raise of pH by conversion of low organic acids was observed in [74]. There was no biogas produced in volumes amenable for measurement between the 2nd and 8th day. After the 9th 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.

A comparison of substrates showed differences of dark fermentation due to pH, substrate, and ranges of OFR that in hydrogen production occurred. The figure proved that lowering of pH in anaerobic digestion of sour cabbage narrows the OFR positive to hydrogen production. 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 [75] 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. [76] (reduction of hydrogen sulfide). It can be discerned that after the 11th day (265 hours) a significant growth of hydrogen production was observed - see Figure 4, due to pH decrease (to 5.1). Similar features can be found in the case of 5 g VSS/L loads but 3 days earlier – Figure 5. 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 was up to 11.19% for 0.58 mL/h (1st day) in the case of 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). The highest hydrogen increments were observed in the first days like in cotton [77] or fruit waste [78]. Thus it did not seem sensible to repeat for lower concentration. This was caused by a higher pH blocking acetogenesis and methane conversion [79]. 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.
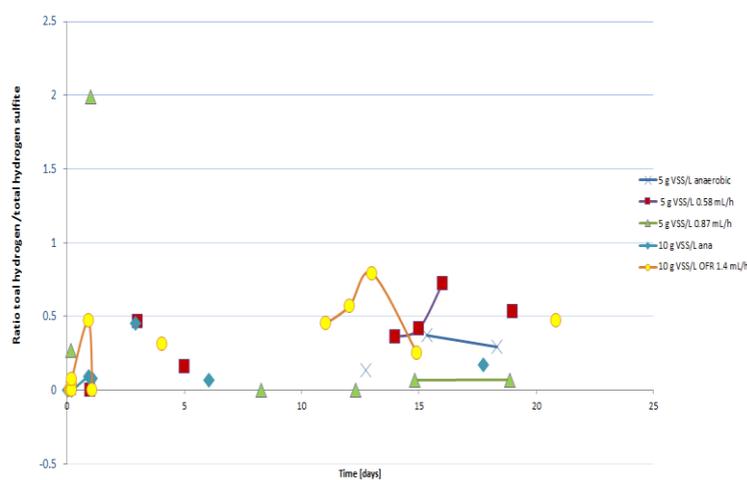
Figure 6. Time evolution ratio of cumulative hydrogen production vs hydrogen sulfide emission

for different concentrations and OFR

The fluctuations of ratios are bigger than in the case [44]. In every case 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 comes 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 sulphide occurred due to the digestion of methionine, however, this was an only small part of the emitted gas.

Table 3: Sulphur added with sour cabbage in samples and the ratio sulphur ratio of sulphur converted in emitted hydrogen sulphide %.

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 (9)

$$C_{400}H_{620}N_{100}O_{120}PS \rightarrow H_2 + CH_4 + CO_2 + C_2H_4 + CH_3OOH + C_2H_5COOH + H_2S \quad (9)$$
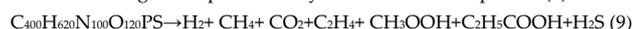
Microaeration for some ranges improves hydrogen production like for cotton [80]. Hydrogen sulphide simultaneously increases but then with OFR raise, it is removed that agrees with [81].

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 [58] lowers the time of digestion. Biogas production in 10 g VSS/L and pH of 6.0 was shorter by two days, see figure 5.

In the case of 10 g VSS/L, the occurrence of the shift of hydrogen production under influence of microaeration, pH, and VSS degree was observed (see Figure 5). It can be discerned the difference of 1 mL of hydrogen between neutral pH [58] and strictly anaerobic at pH 6.0 (19 mL of hydrogen) from sour cabbage [60] (high VSS) if a proper microaeration parameter was used. Higher concentration led to longer hydrogen production, besides acidic pH that shortened time to 15 or 17 days. 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 was just started appearing. The longest and with the highest efficiency was hydrogen production at acidic conditions that agreed with most results [82]. 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 for sour cabbage [83], were almost while for pH 7.5 28 times more methane [58]. 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 gVSS/L.. The increase of OFR influenced negatively methane production from sour cabbage. The increase of substrate resulted in higher hydrogen production that was contrary to the glucose results of Pan et al. [84]. Higher concentration led to longer hydrogen production, however in the case of low pH, only elongated to 4 days more, while in the case of neutral pH 10 days more [58]. An increase in substrate concentration augmented the difference caused by VSS and pH change.

However, in neutral pH with a change of sour cabbage concentration [58], hydrogen yield modified, the concentration of substrates did not affect in alter of hydrogen yield in case of low pH. 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 [75]. Therefore, the availability of substrate 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 OFR 1.4 mL/h for sour cabbage [83], there was made a general percentage of gases during the fermentation in Figure 5.

As we can see in Figure 5 in the case of 10 g VSS/L and OFR 1.4 mL/h, the biogas production length was 22 days; 3 days longer than from 5 g VSS/L. Hydrogen production up to the 4th day was higher than methane production. 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. [85] in wheat straw. Microaeration shortened hydrogen production increasing overall hydrogen yield, therefore converting substrate to hydrogen. The VSS difference did not change time fermentation but a yield of dark fermentation. The most preferable for sour cabbage anaerobic digestion from the investigated value of VSS is VSS 89% can be a special case of ripening with the emission of hydrogen and some ethylene too.

Hydrogen peak day showed the highest hydrogen production from an all-time process. Besides hydrogen peak day, hydrogen production and hydrogen yield were much lower. A similar case was with methane yield and peak day. Hydrogen production was significantly higher from sour cabbage than from key –lime and raw cabbage [75] but remarkably lower than from cassava [86]. This was a result of not using not only the substrate but not additional nutrients like agar plates [51] not additional salts [87]. The results of untreated inoculum give response if treatment was worth like in cotton wastes [80]. Thus promising results showed that it can be interesting additives for substrates that digestion increased pH like proteins [88]. 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]. The process due to high both methane and anaerobic digestion can be classified as dark fermentation or hydrogenotrophic anaerobic digestion.

4. Conclusions

Sour cabbage is a potential source for the production of hydrogen 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 for anaerobic conditions. The flow rate that can improve hydrogen production in the case of 5 g VSS/L feed rate must be higher than 0.58 mL/h and lower than 0.87 mL/h. The maximum methane production was reached under anaerobic conditions. As the oxygen flow rates increased, methane production declines. 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 and in the case, 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 10g VSS/L was up to 22%. Oxygen seems to play the role of a stress factor for bacteria. Proper use of microaeration can be a tool in the stabilization of hydrogen production via dark fermentation or hydrogenotrophic anaerobic digestion. In microaeration conditions besides hydrogen, there can also obtain ethylene which is a raw chemical in polymer chemistry. The phenomena need further research.

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