energies

MDPI

Article

Biogas and Biohydrogen Production Using Spent Coffee Grounds and Alcohol Production Waste

Liana Vanyan [1,2,3], Adam Cenian [4] and Karen Trchounian [1,2,3,*]

[1] Department of Biochemistry, Microbiology and Biotechnology, Faculty of Biology, Yerevan State University, 1 Alex Manoogian Str., Yerevan 0025, Armenia
[2] Scientific Research Institute of Biology, Faculty of Biology, Yerevan State University, Yerevan 0025, Armenia
[3] Microbial Biotechnologies and Biofuel Innovation Center, Yerevan State University, Yerevan 0025, Armenia
[4] Institute of Fluid Flow Machinery, Polish Academy of Sciences, Physical Aspects of Ecoenergy Department, Fiszera 14 Street, 80-231 Gdańsk, Poland
* Correspondence: k.trchounian@ysu.am

Abstract: In this study, alternative uses for lignocellulosic waste by considering them a source of eco-friendly and renewable energy generation with the application of the anaerobic digestion of treated and untreated waste for biogas and biohydrogen generation were investigated. The diluted sulfuric acid method was used for both the substrates and inoculum. Hydrogen production was absent when untreated spent coffee grounds (SCG) and alcohol waste (AW) were both used with the inoculum at pH 5.5 and pH 7.5. Meanwhile, the highest biogas yield of 320 dm^3 kg $V.S^{-1}$ was obtained when using AW at pH 7.5, with a 190 dm^3 kg $V.S^{-1}$ yield of methane. Instead, hydrogen production was observed when initially 4% (*w*/*v*) and 6% (*w*/*v*) SCG-containing hydrolysates were used as the substrates at pH 5.5, yielding 2.9 ± 0.09 dm^3 kg $V.S^{-1}$ and 3.85 ± 0.12 dm^3 kg $V.S^{-1}$, respectively. The further optimization of pretreatment technologies and pH control could lead to increased and prolonged hydrogen production.

Keywords: spent coffee grounds; alcohol waste; biogas; biomethane; biohydrogen

Citation: Vanyan, L.; Cenian, A.; Trchounian, K. Biogas and Biohydrogen Production Using Spent Coffee Grounds and Alcohol Production Waste. *Energies* **2022**, *15*, 5935. https://doi.org/10.3390/en15165935

Academic Editor: Attilio Converti

Received: 10 July 2022
Accepted: 4 August 2022
Published: 16 August 2022

1. Introduction

Nowadays the application of non-conventional fuels using different types of waste or side streams is in great demand. Biogas and biohydrogen are the current best alternatives to fossil fuels. Molecular hydrogen (H_2) is a non-toxic, eco-friendly fuel as only water (H_2O) is generated during its combustion, and it has a ~3.5-time higher energy content than oil, consisting of 142 kJ g^{-1} [1,2]. Biogas consists of methane (50~65%) and carbon dioxide (35~50%), with some additions of hydrogen, nitrogen, ammonia, hydrogen sulfide, and water vapor [3].

Biogas is not a totally pollution-free alternative to fossil fuels but it is considered cleaner than coal [4]. Biogas and biohydrogen production from biomass waste, such as lignocellulosic waste generated in everyday life, could have a significant impact on the world's economy as well as climate change. It is worth mentioning that the global production of lignocellulosic biomass is approximately 120 × 10^9 tons per annum, which is equivalent to 2.2 × 10^{21} J and is four times higher than existing global energy consumption [5]. Globally, a huge amount of waste is generated during the production and consumption of both alcoholic and non-alcoholic beverages. For instance, global beer production exceeded 1.94 billion hL in 2018, of which 85% was brewer's spent grain (BSG) generated as major waste [6]. The worldwide annual production of BSG has been estimated to be approximately 38.6 × 10^6 tons [7]. The total consumption of spirits dipped to 35.27 billion liters in 2020 but is expected to reach almost 38 billion liters by 2025 [8]. Distilleries are one of the most polluting industries as 88% of their raw materials are converted into

waste [9].

On the other hand, a huge amount of waste is also generated from the production of non-alcoholic beverages. In particular, the global consumption of tea surpassed 5.8 million tons in 2019 [10]. Coffee production reached 9542 tons as of 2018 and is continually increasing [11]. Agro-industrial residues, such as brewery spent grains (BSG), coffee waste, sugarcane bagasse, corn cobs, wheat straw, sorghum husks, sorghum leaves, sorghum stover, rice straw, rice bran, and rice husks, used in dark fermentative biohydrogen production using different microorganisms are already well reported [7,12–14]. Anaerobic digestion (decomposition of organic matter under anaerobic conditions by different microbial strains) [15] and dark fermentation are promising solutions for waste-based biogas and biohydrogen production but face challenges, such as finding the optimal pretreatment technology and controlling the pH variations during the culturing of microbial responses to environmental factors [16–18].

Although different microbial strains have the capability for the hydrolysis and degradation of lignocellulosic waste, there is still a need to treat lignocellulosic waste for higher efficiency of anaerobic digestion and dark fermentation. Using some pretreatment methods, the yield of fermentable sugars can reach 90%, which is less than 20% without any pretreatment [19].

Different treatment technologies have been reported for lignocellulosic biomass degradation such as physical/mechanical pretreatment (particle-size reduction, high-pressure homogenization, ultrasonic treatment, gamma-ray irradiation), thermal and hydrothermal treatment, chemical pretreatment, etc., [20].

Acidic pretreatment is one of the most popular pretreatment techniques. Monlau et al. reported a 233 mL CH_4 g^{-1} initial VS yield using HCl as a treating agent at 170 °C for sunflower stalks [21].

Montoya-Rosales et al. reported a more noticeable effect of acidic pretreatment on the solubilization of lignocellulosic compounds than on the biogas yield [22]. Meng et al. also showed enhanced methane production and VS destruction using a free nitrous acid (FNA) pretreatment on thickened waste-activated sludge (TWAS) [23].

The goal of the current research is to understand the applications of anaerobic digestion (AD) of treated and untreated spent coffee grounds (SCG) and alcohol waste (AW) for biogas and biohydrogen generation.

2. Methods

2.1. Batch Culturing

The process of anaerobic digestion was performed in 2 dm^3 wide-mouth bottle DURAN® GLS 80 glass reactors with an active volume of 1.2 dm^3. Glass reactors were tightly connected with water-filled cylindrical vessels for gas collection (Figure 1). Sewage sludge inoculum taken in the summer of 2021 from a wastewater treatment plant in Gdańsk, Poland, was used. As accurate as the experimental setup is harmonized, some variabilities can occur depending on the nature of the used inoculum [24]. In addition, as much as microbial communities inhabiting wastewater treatment or biogas plants are known, the composition and concentration can vary daily or seasonally, thus the simple determination of volatile solids (VS) gives general information about biomass content but other characteristics should be determined perennially [25]. Thus, prior to digestion, total solids [TS] and volatile solids for the inoculum and substrates were determined from the fresh mass [FM] [26] by drying samples in an oven (SLN 115, WODZISŁAW ŚLĄSKI, Poland) at 105 °C for 24 h and later burning for 4–5 h at 550 °C (in a furnace CARBOLITE GERO AAF, Germany).

A 10 g sample of a fresh mass of inoculum was used for volatile solids determination; after drying and periodic weighting, the dry weight was 0.352 g and after burning, the sample weight was 0.117 g. Reactors were set up with a 1 VS substrate/2 VS inoculum ratio, digestion was carried out under mesophilic conditions (40 ± 2 °C), and oxygen was

removed by flashing the rectors with nitrogen. The pH value was monitored once a day using a combination pH electrode (IJ44A, ELMETRON, Poland).

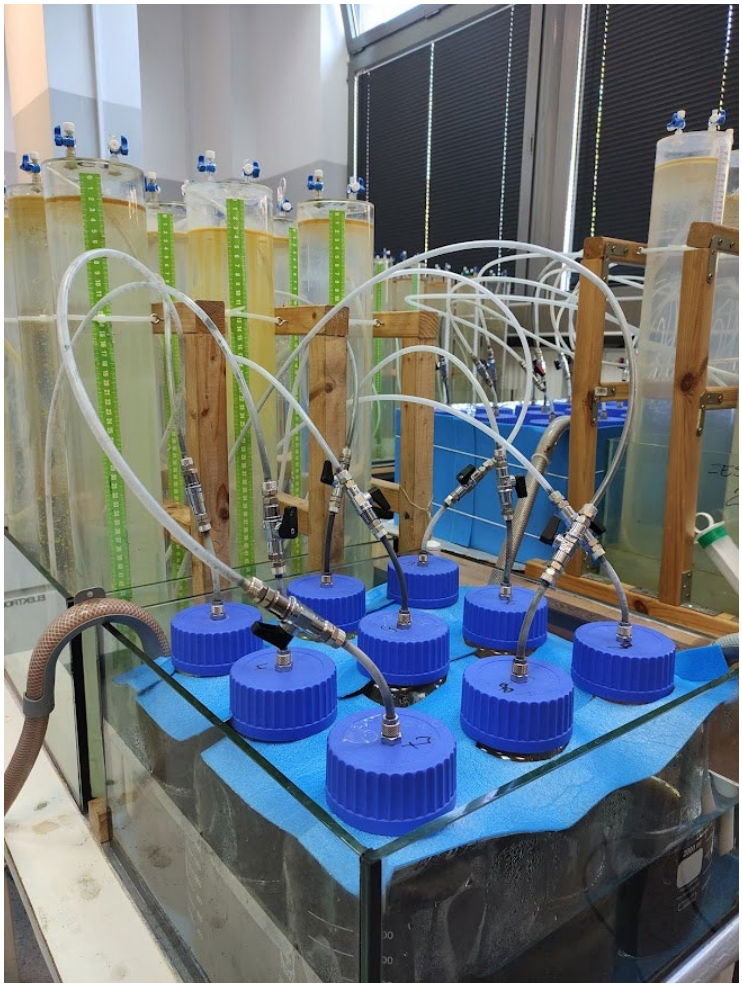


Figure 1. Experimental setup for anaerobic digestion.

2.2. Feedstock, Treatment, and Medium Preparation

Spent coffee grounds (SCG) that were sourced from a coffee shop (in the Institute of Fluid-Flow Machinery) and the alcohol waste from Pomeranian Voivodship (a distillery that processes potatoes into alcohol) were used as a feedstock representing the two types of big industrial waste, non-alcoholic and alcoholic beverages, respectively. The used alcohol waste consisted of potato stillage—a mixture of water, yeast, enzymes, starch, alcohols, fermentation additives, and potato residues. From the existing physical, chemical, thermochemical, and biological methods of waste treatment [27], acidic (chemical) pretreatments had been beneficially preferred. Lignocellulosic waste was used both with and without treatment by either suspending it in distilled water and exposing it to pretreatment with acidic hydrolysis at 121°C for 45 min or by directly adding the required amount to the reactor. Various waste concentrations were tested: 4% (*w*/*v*) and 6% (*w*/*v*) of SCG treated with 0.4% (*v*/*v*) sulfuric acid [12], as well as 10% (*w*/*v*) and 20% (*w*/*v*) of AW treated with 1.5% (*v*/*v*) sulfuric acid [28]. Later, the substrate's low pH was adjusted to proper fermentation conditions either with potassium hydroxide KOH or with monopotassium phosphate (KH_2PO_4).

The pH of the inoculum for biogas production was not adjusted as naturally, it is at around 7.5 (Table 1), but for biohydrogen production, it was adjusted to 5.5 by using concentrated sulfuric acid (95%).

Table 1. The composition and characteristics of wastes and inoculum used in this study.

Material	pH	Consistency	TS [%FM]	VSS [%TS]
Inoculum	7.5	liquid	3.52	69.00
Coffee waste without treatment	-	solid	41.58	97.53
4% (*w*/*v*) coffee waste treated with 0.4% (*v*/*v*) sulfuric acid	1–2	liquid	1.98	92.31
6% (*w*/*v*) coffee waste treated with 0.4% (*v*/*v*) sulfuric acid	1–2	liquid	2.72	91.86
Alcohol waste without treatment	5	liquid	3.27	86.81
10% (*w*/*v*) AW treated with 1.5% (*v*/*v*) sulfuric acid	1–2	liquid	3.48	80.21
20% (*w*/*v*) AW treated with 1.5% (*v*/*v*) sulfuric acid	1–2	liquid	3.80	95.85

2.3. Gas Analysis

The volume of gases produced was measured every day by collecting them in cylindrical vessels. The qualitative and quantitative assessments of the gases were performed using a portable biogas analyzer (GA5000, Geotech, Dexter, MI, USA) for methane determination and using a gas chromatograph (GC) with a thermal conductivity detector and argon as a carrier for biohydrogen determination using the GC parameters of a stainless steel column of 2.0 m × 2.2 mm I.D. × 1/8-inch O.D., Shincarbon-ST 50/80. The gas flow rate was 0.6 mL/h; the run started at 40 ^{O}C, which was held for 2.5 min, and then the temperature was increased to 180 °C with a 35 °C /min rate and held for the next 1.5 min. The gas analyzer allowed the measurements of CH_4, CO_2, O_2, H_2, and H_2S in the ranges 0–100%, 0–100%, 0–25%, 0–1000 ppm, and 0–5000 ppm, respectively [27]. Daily records of room temperature, actual pressure, and absolute pressure in a tube were collected and further recalculated according to normal conditions. Biogas production was observed continuously for 25 days and biohydrogen production for 10 days.

2.4. Reagents and Data Processing

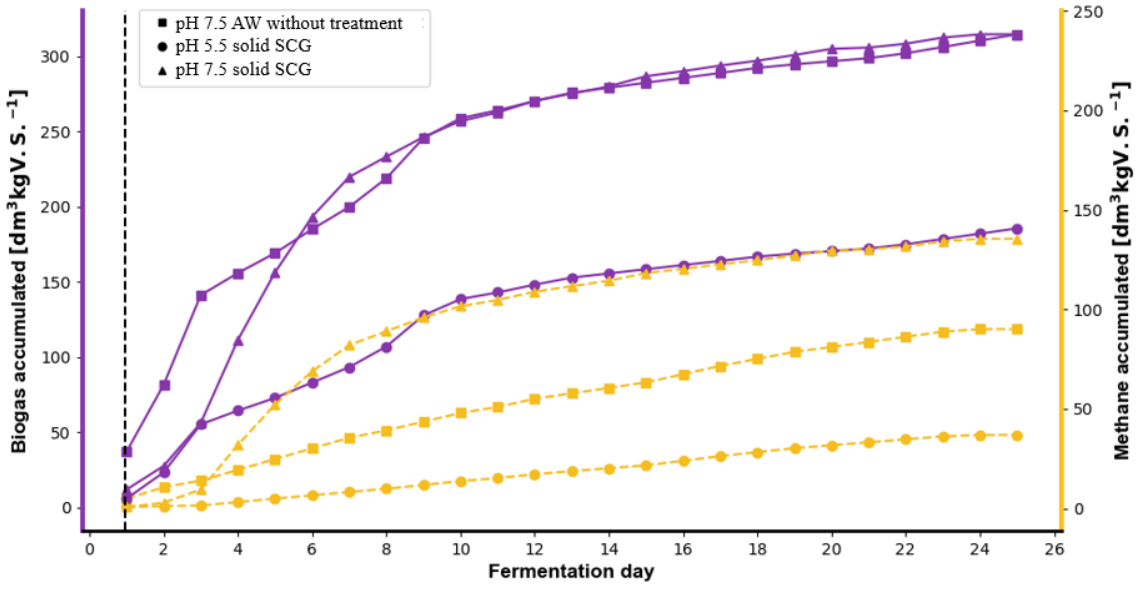
K_2HPO_4, KOH, H_2SO_4, and other reagents of analytical grade were used. Each data point represented was averaged from independent triplicate cultures; the standard deviation calculated according to [12,29] was not more than 3% if it is not presented. The average of the data was calculated by performing at least three experiments; the standard errors were considered, and reactors containing only the inoculum and feedstock were set up to observe the amount of gas produced by their mixture.

3. Results and Discussion

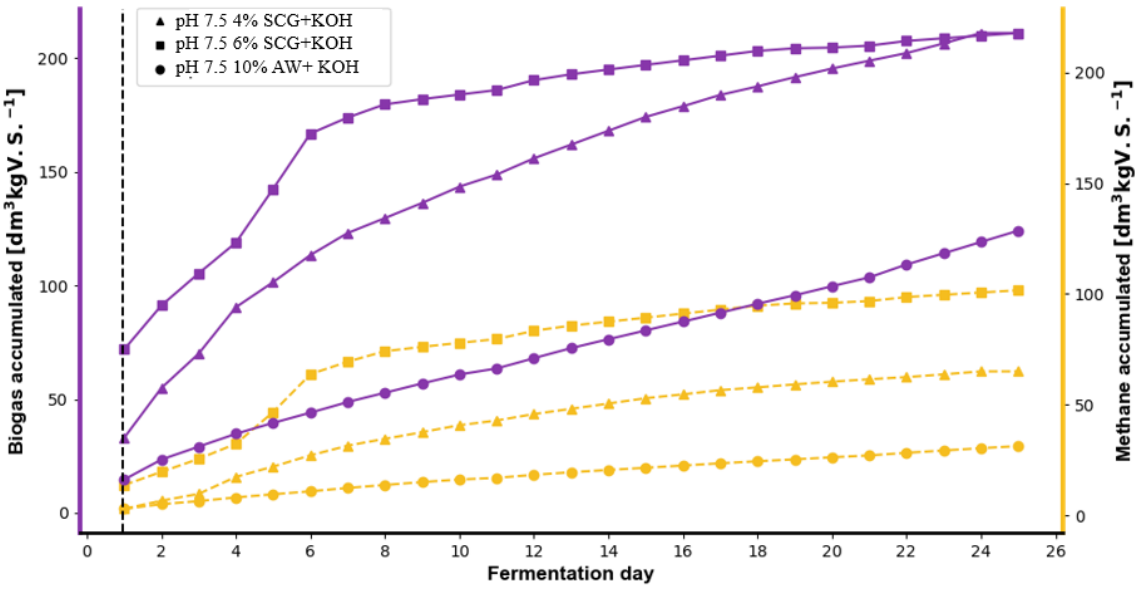
3.1. Biogas and Biohydrogen Production from SCG and AW

All the analyses were conducted in batch systems: substrates and inoculum were added once to the digester for the duration of the process. The data in Table 1 show that the SCG and AW are promising substrates with high organic content; therefore, their use could be the basis for the increased and cost-effective production of biogas and biohydrogen. The biogas and methane yields were higher for the untreated than for the pretreated waste; however, the opposite was observed in the case of biohydrogen generation: waste treatment improved biohydrogen production. The highest biogas yield was observed for the SCG without treatment and inoculum at pH 7.5; on the fourth day of fermentation, the yield was 41.7 dm^3 kg $V.S^{-1}$ and the actual methane content was ~50%, reaching 70% at the end of the digestion process. The cumulated biogas was 238 dm^3 kg $V.S^{-1}$ (Figure 2a), which was equal to 182 dm^3 kg dry $matter^{-1}$ (data not shown).

When the AW was used as a feedstock without treatment under the same conditions, the biogas and methane yields were comparatively higher: the accumulated biogas was 320 dm^3 kg $V.S^{-1}$, with the highest yield of 60 dm^3 kg $V.S^{-1}$ on the third day of digestion. Moreover, the actual methane content was higher reaching 75% at the end of the digestion process. Respectively, the total biogas and methane generation was 135 dm^3 kg $V.S^{-1}$ and 190 dm^3 kg $V.S^{-1}$ (Figure 2a). Similar methane yield was obtained by Luz et al. (2017) using SCG and fresh cow manure [30]. As shown in Table 2, depending on the treatment technology and inoculum used, different methane yields were obtained [31–34].



(**a**)



(**b**)

Figure 2. Accumulation of biogas (violet) and methane (yellow) during 25 days of fermentation during utilization of (**a**) untreated and (**b**) pretreated SCG and AW.

Table 2. Comparative table of methane and hydrogen yields.

Substrate	Inoculum	Cumulative H_2 Volume Dm^3 Kg $V.S^{-1}$	Cumulative CH_4 Volume Dm^3 Kg $V.S^{-1}$	Biogas Volume Dm^3 Kg $V.S^{-1}$	Reference
Boll pretreated with 8% (*w*/*w*) sodium hydroxide solution for 10 min at 100 °C.	Wastewater treatment sludge heat-shocked at 85 °C for 45 min	17.1	246.4	-	[35]
Native consortium of microalgal biomass without treatment	Treated anaerobic sludge	15.0	245	-	[36]
SCG	a liquid fraction of pig manure	-	290	-	[31]
SCG pretreated with 8% NaOH	Granular sludge (5.2 g VS/L, VS/TS ratio = 0.6) collected from a full-scale upflow anaerobic sludge blanket (UASB) digester of a brewery factory	-	392	-	[32]
''coffee'' waste from instant coffee substitute production	The granular sludge collected from a UASB (upflow anaerobic sludge blanket) reactor treating brewery effluent	-	280	-	[33]
Coffee husks harvested from agricultural land in the municipality of Lavras. Pretreatment at 120 °C for 60 min	Microalgal biomass was harvested from a full-scale wastewater treatment raceway pond	-	196	-	[34]
Spent coffee water	fresh cow manure	-	167.80	-	[30]
Cotton waste	Inoculum from a mesophilic digester mainly used to treat maize silage and manure	1.1	780	-	[26]
Alcohol waste without treatment	Sewage sludge from wastewater treatment plant	-	135	240	This study
SCG without treatment	Sewage sludge from wastewater treatment plant	-	190	320	This study
SCG treated with 0.4% sulfuric acid	Sewage sludge from wastewater treatment plant	3.85	1.3	43	This study

On the other hand, it is well known that commercial biogas plants typically produce biogas with a CH_4 content of 50–70% [37]. Thus, it can be stated that the obtained data are promising for the commercialization and further application of SCG and AW and the development of new biogas stations in Armenia, as methane content with a high upper limit was generated. Interestingly when the inoculum with a pH of 5.5 was applied, the biogas yield from the SCG was 118.4 dm^3 kg $V.S^{-1}$ with a maximum methane content of

50%, but no significant gas generation was observed when using the AW (data not shown).

During the SCG digestion at pH 7.5, the pH value decreased by ~0.5 during the first week and slowly increased to pH 7.8 at the end of the process. However, when AW was used, the changes in the pH were not significant. In contrast, when a pH of 5.5 was applied as a result of the degradation of the SCG, the pH significantly increased to pH 7 (Figure 3) and thus the methane production advanced instead of the desired hydrogen. In addition, no significant pH changes were observed during the digestion of untreated AW at pH 5.5.

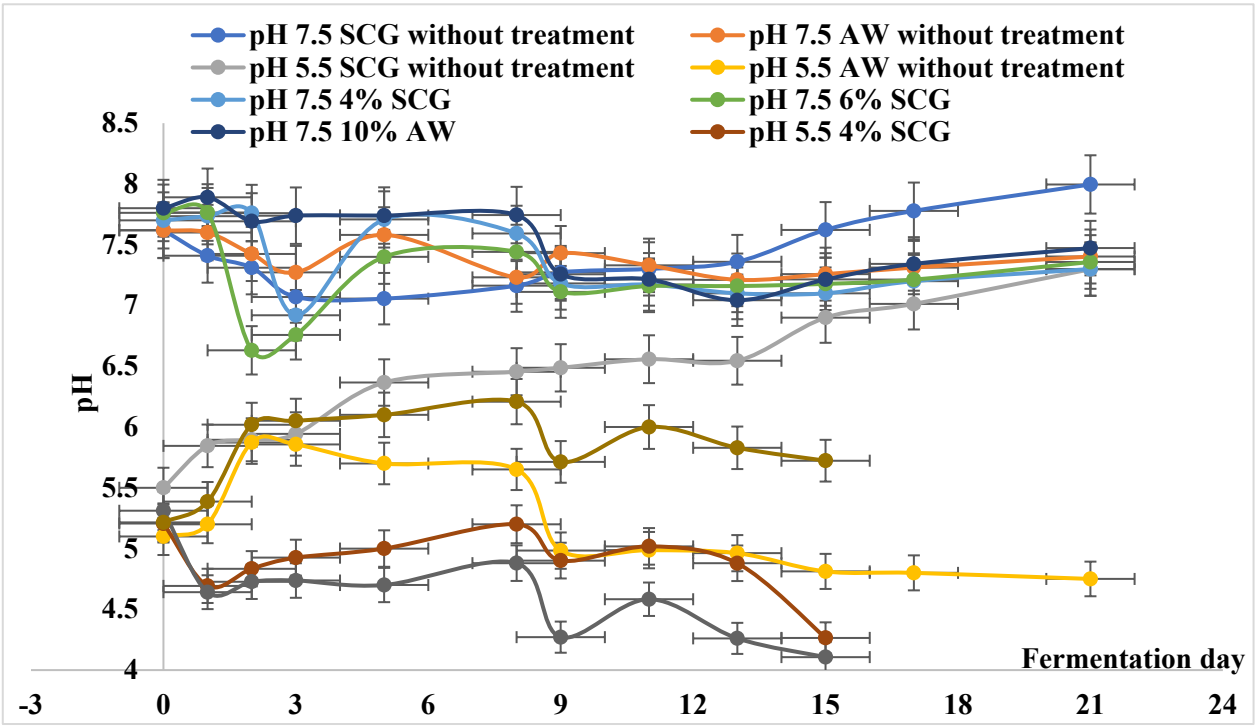


Figure 3. pH changes during batch culturing containing treated and untreated SCG and AW as a substrate. For details, see Materials and Methods section.

3.2. The Effect of Pretreatment on Biogas and Biohydrogen Production

As mentioned above, the investigated lignocellulosic waste underwent some pretreatment to examine its influence on biogas and biohydrogen production. Initially, 4% and 6% SCG-containing medium were suspended in a slightly acidic (0.4% sulfuric acid) solution, after which medium filtration and pH adjustment, either with potassium hydroxide (KOH) or dipotassium hydrogen phosphate (K_2HPO_4), were performed. Petrosyan et al. [12] have shown that media pH adjustment using K_2HPO_4 is optimal for biohydrogen production when using a pure culture of *E. coli.* Interestingly, in our study, this principle was inefficient for both biogas and biohydrogen production, which can be explained due to the generation of inhibiting factors during both hydrolysis and gas generation (data not shown). The inhibiting factors could be the result of thermal treatment or hemicellulose hydrolysis. The generation of dangerous compounds because of the dehydration of xylose galactose, mannose, and glucose-like furfural, hydroxymethylfurfural, and phenolic acids could have occurred. Nevertheless, the generation of inhibitory substances, such as phenolics, furfurals, and aldehydes, means this type of *pH* adjustment is not preferable as it is influenced by the acid concentration, reaction temperature, etc., [19].

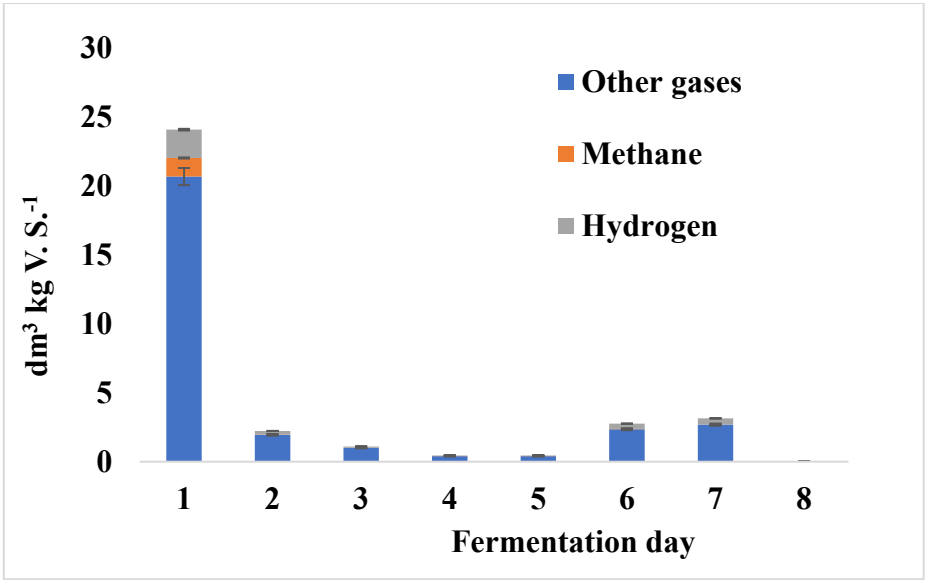
A pH adjustment using KOH was more optimal than using K_2HPO_4; namely, the biogas yields were 218 dm^3 kg $V.S^{-1}$ and 212 dm^3 kg $V.S^{-1}$ (Figure 2b), respectively, when 4% and 6% SCG-containing mediums were applied in the AD process.

It is clear that the concentration of SCG does not affect general biogas production; however, it has a positive effect on the generated methane amount; when a 4% SCG medium was applied, the accumulated methane yield was ~65 dm^3 kg $V.S^{-1}$, but the 6% SCG medium resulted in a higher (100 dm^3 kg $V.S^{-1}$) methane yield (Figure 2b). When using the 4% SCG medium, the highest methane production was observed on the fifth day of fermentation. Meanwhile, during digestion of the 6% SCG-containing medium, these results were obtained on the sixth day of fermentation. It is worth mentioning that out of all of the tested AW concentrations, to some extent significant gas production was observed only when using a 10% concentration, with a 140 dm^3 kg $V.S^{-1}$ accumulated biogas yield and 32 dm^3 kg $V.S^{-1}$ accumulated methane yield (Figure 2b). These data are lower compared to the untreated AW, showing that in this case, crude feedstock leads to the highest biogas yields.

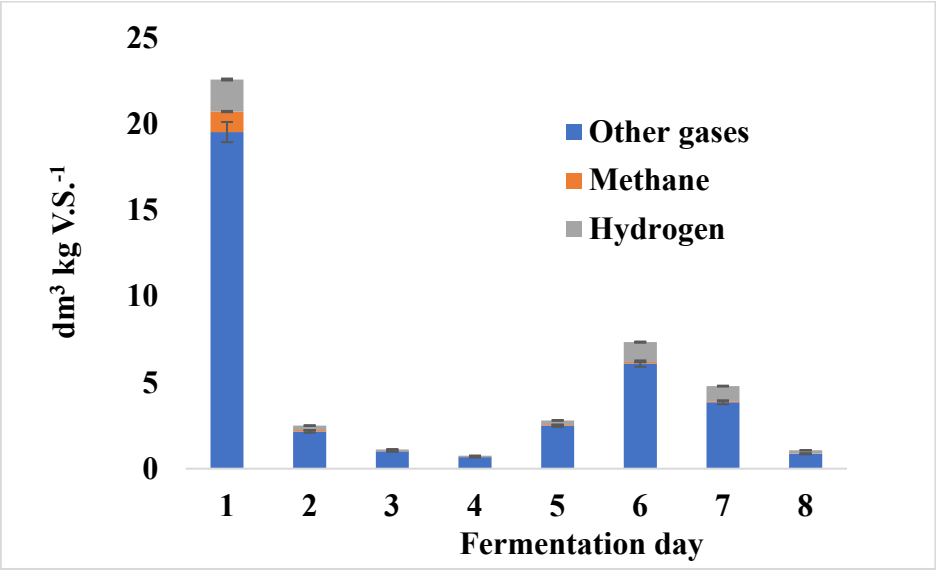
Promising data were obtained for hydrogen production during the utilization of treated SCG at pH 5.5. Hydrogen generation has been extensively studied for a broad variety of lignocellulosic substrates [38]. One of the main limitations of H_2 production from agricultural residues is the low biodegradability of lignocellulosic materials, thus the possibility of acidic hydrolysis has been investigated.

In this case, the pH adjusting agent also did not have any significant effect (data not shown) and further investigations were carried out using KOH. During the fermentation of treated 4% and 6% mediums containing SCG hydrolysate in both cases, the highest hydrogen production was observed on the first day of fermentation, namely, 2.05 dm^3 kg $V.S^{-1}$ (Figure 4a) and 1.86 dm^3 kg $V.S^{-1}$ (Figure 4b), respectively.

Generally, a high H_2 production rate could lead to a fast dark fermentative medium with highly acidic conditions due to the large amount of produced acidic metabolites, e.g., acetic, butyric, malic, propionic, fumaric, and succinic acids [38]. For instance, during the dark fermentation of 4% and 6% SCG medium-containing reactors, the pH dropped by 4.5 after the first day of fermentation, but interestingly, on the sixth and seventh days of fermentation, an increase in the pH to ~5.2 was observed, which consequently resulted in a hydrogen generation, especially in the 6% SCG-containing reactors, of ~1.2 dm^3 kg $V.S^{-1}$ (Figure 4b). This fact once again underscores the importance of pH management for the optimal production and high yield of H_2 [39].



(**a**)



(b)

Figure 4. Daily hydrogen production of treated 4% (**a**) and 6% (**b**) SCG during 8 days of fermentation at pH 5.5. For details see the Materials and Methods section.

The usage of a 6% SCG-containing medium was more optimal for the total cumulated hydrogen yield, which was 3.85 dm^3 kg $V.S^{-1}$, comparatively 1.4-fold higher than for the yield from the 4% SCG-containing substrate. This is higher compared to the results obtained from using cotton waste [21]; however, it is somewhat inferior to the data obtained for other types of waste [32,33]. These results suggest that the improved hydrogen yield correlates well with the increase in the soluble sugar and lignin removal. During fermentation of the 6% SCG-containing medium, the cumulated biogas yield was 43 dm^3 kg $V.S^{-1}$. Untreated or treated AW was not efficient for biohydrogen production.

4. Conclusions

It can be concluded that SCGs and AW are promising substrates for bioenergy production. The results obtained indicate that acidic hydrolysis treatment was important for biohydrogen but not for biogas production. The highest biogas yield of 320 dm^3 kg $V.S^{-1}$ was observed when untreated AW with an inoculum at pH 7.5 was used. However, the highest hydrogen yield of 3.85 dm^3 kg $V.S^{-1}$ was observed in batch cultures containing a 6% SCG hydrolysate with an inoculum at pH 5.5.

Author Contributions: Conceptualization, L.V. and K.T.; methodology, A.C. and K.T.; software, L.V.; validation, L.V. and A.C.; formal analysis, L.V. and K.T.; investigation, L.V.; resources, A.C.; data curation, A.C.; writing—original draft preparation, L.V. and K.T.; writing—review and editing, A.C. and K.T.; visualization, A.C.; supervision, A.C. and K.T.; project administration, K.T.; funding acquisition, L.V. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by the COST Action "Understanding and exploiting the impacts of low pH on microorganisms" (EuroMicropH) CA18113. L.V. visited the AC laboratory as the recipient of a Short-Term Scientific Mission grant supported by the COST Action CA18113 EuroMicropH. This work was also supported by a research grant from the Science Committee of the Ministry of Education, Science, Culture, and Sports of Armenia (21AG-1F043).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Trchounian, K.; Trchounian, A. Hydrogen production from glycerol by *Escherichia coli* and other bacteria: An overview and perspectives. *Appl. Energy* **2015**, *156*, 174–184.
2. Mahmoodi-Eshkaftaki, M.; Mockaitis, G. Structural optimization of biohydrogen production: Impact of pretreatments on volatile fatty acids and biogas parameters. *Int. J. Hydrogen Energy* **2022**, *47*, 7072–7081.
3. Abrahama, A.; Mathewa, A.K.; Parka, H.; Choia, O.; Sindhub, R.; Parameswaranb, B.; Pandeyc, A.; Parkd, J.H.; Sanga, B.-In. Pretreatment strategies for enhanced biogas production from lignocellulosic biomass. *Bioresour. Technol*. **2020**, *301*, 122725.
4. Bharathiraja, B.; Sudharsana, T.; Jayamuthunagai, J.; Praveenkumar, R.; Chozhavendhan, S.; Iyyappan, J. Biogas production–A review on composition, fuel properties, feed stock and principles of anaerobic digestion. *Renew. Sust. Energ. Rev.* **2018**, *90*, 570–582.
5. Guo, M.; Song, W.; Buhainc, J. Bioenergy and biofuels: History, status, and perspective. *Renew. Sust. Energ. Rev.* **2015**, *42*, 712–725.
6. Rachwał, K.; Waśko, A.; Gustaw, K.; Polak-Berecka, M. Utilization of brewery wastes in food industry. *Peer J.* **2020**, *8*, 9427.
7. Poladyan, A.; Trchounian, K.; Vassilian, A.; Trchounian, A. Hydrogen production by *Escherichia coli* using brewery waste: Optimal pretreatment of waste and role of different hydrogenases. *Renew. Energy* **2018**, *115*, 931.
8. Available online: https://www.statista.com/forecasts/232925/volume-of-global-spirit-consumption (accessed on 9 July 2022).
9. Kharayat, Y. Distillery wastewater: Bioremediation approaches. *J. Integr. Environ. Sci.* **2012**, *9*, 69–91.
10. Guo, S.; Kumar, A.M.; Wang, Y.; Xu, P. Current understanding in conversion and application of tea waste biomass: A review. *Bioresour. Technol*. **2021**, *338*, 125530.
11. Yun, B.Y.; Cho, H.M.; Kim, Y.U.; Lee, S.C.; Berardi, U.; Kim, S. Circular reutilization of coffee waste for sound absorbing panels: A perspective on material recycling. *Environ. Res.* **2020**, *184*, 109281.
12. Petrosyan, H.; Vanyan, L.; Mirzoyan, S.; Trchounian, A.; Trchounian, K. Roasted coffee wastes as a substrate for *Escherichia coli* to grow and produce hydrogen. *FEMS Lett.* **2020,** 367, fnaa088.
13. Wang, J.; Yin, Y.; Progress in microbiology for fermentative hydrogen production from organic wastes. *Crit. Rev. Environ. Sci. Tec.* **2019**, *49*, 1–41.
14. Raghulchandrana, R.; Tamizhini, A.; Snehya, A.V.; Pandey, R.P.; Raghulchandrana, R.; Tamizhini, A.; Snehya, A.; Pandey, R.P. Pretreatment Studies of Biohydrogen Production from Agro-Industrial Waste. *Preprints* **2020**, 2020110320. doi:10.20944/preprints202011.0320.v1
15. Chen, Y.; Cheng, J.J.; Creamer, K.S. Inhibition of anaerobic digestion process: A review. *Bioresour. Technol*. **2008**, *99*, 4044–4064.
16. Wei, H.; Junhong, T.; Yongfeng, L. Utilization of food waste for fermentative hydrogen production. *Phys. Sci. Rev.* **2016**, *1*, 20160050.
17. Sekoai, P.T.; Daramola, M.O. Effect of metal ions on dark fermentative biohydrogen production using suspended and immobilized cells of mixed bacteria. *Chem. Eng. Commun.* **2018**, *205*, 1011–1022.
18. Trchounian, K.; Sawers, R.G.; Trchounian, A. Improving biohydrogen productivity by microbial dark- and photo-fermentations: Novel data and future approaches. *Renew. Sust. Energ. Rev.* **2017**, *80*, 1201–1216.
19. Rezania, S.; Din, M.F.M.; Mohamad, S.E.; Sohaili, J.; Taib, S.M.; Yusof, M.B.M.; Kamyab, H.; Darajeh, N.; Ahsan, A. Review on Pretreatment Methods and Ethanol Production from Cellulosic Water Hyacinth. *BioResources* **2017**, *12*, 2108–2124.
20. Kamperidou, V.; Terzopoulou, P. Anaerobic Digestion of Lignocellulosic Waste Materials. *Sustainability* **2021**, *13*, 12810.
21. Monlau, F.; Barakat, A.; Steyer, J.P.; Carrere, H. Comparison of seven types of thermo-chemical pretreatments on the structural features and anaerobic digestion of sunflower stalks. *Bioresour. Technol*. **2012**, *120*, 241–247.
22. Montoya-Rosales, J.J.; Peces, M.; González-Rodríguez, L.M.; Alatriste-Mondragón, F.; Villa-Gómez, D.K. A broad overview comparing a fungal, thermal and acid pre-treatment of bean straw in terms of substrate and anaerobic digestion effect. *Biomass Bioenergy* **2020**, *142*, 105775.
23. Meng, J.; Duan, H.; Li, H.; Watts, S.; Liu, P.; Shrestha, S.; Zheng, M.; Yu, W.; Chen, Z.; Song, Y.; et al. Free nitrous acid pre-treatment enhances anaerobic digestion of waste activated sludge and rheological properties of digested sludge: A pilot-scale study. *Water Res.* **2020**, *172*, 115515.
24. Blok, J.; De Morsier, A.; Gerike, P. Harmonisation of ready biodegradability tests. *Chemosphere* **1985**, *14*, 1805–1820.
25. Raposo, F.; De la Rubia, M.A.; Fernández-Cegrí, V.; Borja, R. Anaerobic digestion of solid organic substrates in batch mode: An overview relating to methane yields and experimental procedures. *Renew. Sust. Energ. Rev.* **2012**, *16*, 861–877.
26. 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.
27. Taylor, M.J.; Alabdrabalameer, H.A.; Skoulou, V. Choosing Physical, Physicochemical and Chemical Methods of Pre-Treating Lignocellulosic Wastes to Repurpose into Solid Fuels. *Sustainability* **2019**, *11*, 3604.
28. Mirzoyan, S.; Toleugazykyzy, A.; Bekbayev, K.; Trchounian, A.; Trchounian, K. Enhanced hydrogen gas production from mixture of beer spent grains (BSG) and distiller's grains (DG) with glycerol by *Escherichia coli*. *Int. J. Hydrog. Energy* **2020**, *45*, 17233–17240.
29. Trchounian, K.; Sanchez-Torres, V.; Wood, T.K.; Trchounian, A. *Escherichia coli* hydrogenase activity and H2 production under glycerol fermentation at a low pH. *Int. J. Hydrog. Energy* **2011**, *36*, 4323–4331.
30. Luz, F.C.; Cordiner, S.; Manni, A.; Mulone, V.; Rocco, V. Anaerobic digestion of coffee grounds soluble fraction at laboratory scale: Evaluation of the biomethane potential. *Appl. Energy* **2017**, *207*, 166–175.

31. Vasmara, C.; Marchetti, R. Spent coffee grounds from coffee vending machines as feedstock for biogas production. *Environ. Eng. Manag. J.* **2018**, *17*, 2401–2408.
32. Girotto, F.; Lavagnolo, M.C.; Pivato, A. Spent Coffee Grounds Alkaline Pre-treatment as Biorefinery Option to Enhance their Anaerobic Digestion Yield. *Waste Biomass Valor* **2018**, *9*, 2565–2570.
33. Neves, L.; Oliveira, R.; Alves, M.M. Anaerobic co-digestion of coffee waste and sewage sludge. *J. Waste Manag.* **2006**, *26*, 176–181.
34. Passos, F.; Cordeiro, P.H.M.; Baeta, B.E.L.; de Aquino, S.F.; Perez-Elvira, S.I. Anaerobic co-digestion of coffee husks and microalgal biomass after thermal hydrolysis. *Bioresour. Technol.* **2018**, *253*, 49–54.
35. Ghasemian, M.; Zilouei, H.; Asadinezhad, A. Enhanced Biogas and Biohydrogen Production from Cotton Plant Wastes Using Alkaline Pretreatment. *Energy Fuels* **2016**, *30*, 10484–10493.
36. Carrillo-Reyes, J.; Buitrón, G. Biohydrogen and methane production via a two-step process using an acid pretreated native microalgae consortium. *Bioresour. Technol*. **2016**, *221*, 324–330.
37. Adnan, A.I.; Ong, M.Y.; Nomanbhay, S.; Chew, K.W.; Show, P.L. Technologies for biogas upgrading to biomethane: A review. *Bioengineer* **2019**, *6*, 9.
38. Dimitrellos, G.; Lyberatos, G.; Antonopoulou, G. Does Acid Addition Improve Liquid Hot Water Pretreatment of Lignocellulosic Biomass towards Biohydrogen and Biogas Production? *Sustainability* **2020**, *12*, 8935.
39. Cetecioglu, Z.; Atasoy, M.; Cenian, A.; Sołowski, G.; Trcek, J.; Ugurlu, A.; Sedlakova-Kadukova, J. Bio-Based Processes for Material and Energy Production from Waste Streams under Acidic Conditions. *Fermentation* **2022**, *8*, 115.