Research Article

Alternative methods for dark fermentation course analysis

Edyta Słupek[1] · Karolina Kucharska[1] · Jacek Gębicki[1]

Abstract
Dark fermentation course analysis is crucial, as complexed matrix of gaseous components may be formed and revealed during the process. The paper considers key issues related to the microbiological process in which complex organic substances are transformed into hydrogen. For the purposes of hydrogen generation, the application of wastewater mixed sludge pre-treated according to Faloye method (Faloye et al. in Int J Hydrog Energy 38:11765–11773, 2013. https://doi.org/10.1016/j.ijhydene.2013.06.129; Int J Hydrog Energy 39:5607–5616, 2014. https://doi.org/10.1016/j.ijhydene.2014.01.163) was applied. The main risk of by-product formation is related to the presence of methanogens, i.e., *Archea*, in the sludge. The application of gaseous chromatography confirmed the presence of hydrogen during the initial, lag and log phases of the culture and methane in the late logarithmic death phase of the culture. However, other fermentation gaseous products' presence was not confirmed, as their concentration was under the limit of detection. Therefore, a revision regarding the application of matrix sensors was proposed, and the levels of gases able to be measured using both gas chromatography and matrix sensors were conducted. The criteria of matrix sensors' selection should include the selectivity not only for the hydrogen, hydrogen sulfide or methane, but also the sensitivity to the response of other gases contained in the mixture—ammonium, carbon dioxide and oxygen. A comprehensive combination of commercially available sensors and their applicability for the purposes of dark fermentation course analysis was presented on the basis of the levels of gas concentrations in the generated gas mixture.

Keywords Dark fermentation · Matrix sensors · Biogas · Hydrogen · Bioconversion

1 Introduction

Fermentation is a group of biological process of decomposition of organic substances leading to stabilization of sewage sludge, waste materials and residues. Diversified phenomena occur during fermentation processes, as a result of the entire range of organic compounds degradation with the formation of, that is, methane, ethanol or hydrogen and carbon dioxide [3–5]. Currently, fermentation is used in four main sectors of waste processing including treatment of urban wastewater, agricultural waste, food and biomass industries and processing of the organic fraction of municipal solid waste [5–7]. Biomass residues of wide origin are considered as great potential materials for biofuels production [3, 8, 9]. The main directions in biomass to biofuels transformation are presented in Fig. 1.

The objective of this paper is the research on dark fermentation to biohydrogen and the factors affecting this process. Hydrogen is the most widespread element in nature. Non-renewable fossil raw materials such as crude oil (about 50%), natural gas (30%) and coal (15%) [10, 11] are the most commonly used sources for hydrogen production. Among the leading technologies for hydrogen production using conventional energy sources are steam reforming of natural gas and crude oil, the catalytic decomposition of natural gas, partial oxidation of heavy hydrocarbon fractions of crude oil and gasification of coal or coke. Unfortunately, these methods are

✉ Edyta Słupek, edyta.slupek@pg.edu.pl | [1]Department of Process Engineering and Chemical Technology, Faculty of Chemistry, Gdańsk University of Technology, Narutowicza 11/12 Street, 80-233 Gdańsk, Poland.

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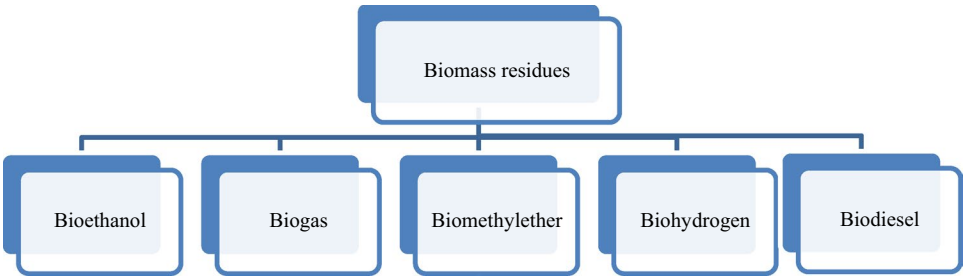

Fig. 1 Main directions in biomass to biofuels transformation

highly energy-intensive, require the use of high temperatures (> 700 °C) and pollute the environment due to the carbon, sulfur and nitrogen oxides emission [12, 13]. Another important industrial process for the production of hydrogen is the electrolysis of water, under the influence of electric current. This method, however, requires delivery of electricity from coal and natural gas or nuclear power plants. Therefore, non-renewable fossil fuels are used indirectly as raw materials. It is estimated that the cost of electricity represents about 80% of the total cost of the process [14], and the production of hydrogen by electrolysis of water is currently about 3.5 times more expensive compared to natural gas steam reforming [15]. The advantage of electrolysis is, however, no emission of carbon dioxide into the atmosphere. Other hydrogen production methods, such as thermochemical or photocatalytic decomposition of water and a high-temperature plasma technology separation of hydrocarbons into hydrogen and carbon, are the subject of intensive research into their development.

Hydrogen conversion from biomass may be a good alternative if biotechnological methods are used. The biological technologies of producing hydrogen include processes involving light energy: direct and indirect biophotolysis and photofermentation. The second group are the biological processes in the absence of light: dark fermentation, bioelectrolysis and bioconversion of carbon monoxide [16]. The dark fermentation is considered as the most promising method for biological hydrogen production. Carbohydrate substrates are converted in the absence of light by bacteria in the process of anaerobic respiration. The raw materials for the fermentation may be glycerin or simple sugars as well as cellulose or starch, which can be hydrolyzed to monosaccharides [17, 18]. In particular, it is desirable to use by-products, waste products rich in glycerol, starch and cellulose from agri-food, wood and paper industries to produce the second-generation biohydrogen using microbial metabolic processes. While the biomass contains high amounts of polysaccharides, which can be processed into hydrogen, it be an alternative to currently used processes, such as combustion or composting. Utilization of waste products that are difficult to dispose can contribute to environmental protection through both more rational use of natural resources and reducing the environmental load of such waste.

The first step in dark fermentation is glycolysis—glucose is fermented to pyruvate. Pyruvate is oxidized and transfers the electrons to ferredoxin [19]. Hydrogenase enzyme catalyzes the reduction of protons to hydrogen, using electrons from ferredoxin. The two types of fermentation pathways are distinguished depending on which chemical compound is the main product. *Bacillus* and *Enterobacter* species have the ability to metabolize via mixed acid fermentation [20–22]. In this case, butyric acid, butanol, hydrogen, carbon dioxide, acetic acid and other compounds such as acetone may be formed. Generation of a variety of final products decreases the amount of formed hydrogen. Theoretically stoichiometric amount of hydrogen produced during the complete decomposition of 1 mol of glucose may be equal to 12 mol (Eq. 1).

$$C_6H_{12}O_6 + 6H_2O \rightarrow 12H_2 + 6CO_2 \quad (1)$$

Many factors such as inoculum, substrates, inorganic nutrients, reactor type and operational conditions like temperature and pH influence on the dark fermentation process course [23, 24]. Depending on the factors, different courses of fermentation may occur. When pure bacterial cultures are used, hydrogen is the main product during fermentation. However, using different types of inoculum, i.e., mixed sludge, causes a risk of infection even if the inoculum is prepared according to the procedures described in the literature [1, 2].

Considering all the analytical problems that are encountered in gas analysis during dark fermentation, there is a growing interest in analytical tools that can identify and determine the amount and composition of emerging gases online. Till now, gas analysis is usually based on sampling and laboratory analysis via gas chromatography (GC) [25, 26]. However, this approach may be time-consuming and expensive. A comparison of analytical- and sensor-based methods for gas analysis is given in Table 1.

In the monitoring of gaseous/odorogenic compounds, primarily olfactometry is used. This is a method of quantifying the aromatic concentration expressed in European fragrances in a cubic meter using an instrument called an olfactometer [27]. Gas chromatography is another

Table 1 Comparison of procedure complexity of analytical- and sensor-based approach

Parameters	Analytical instrument (i.e., GC)	Gas sensors
Process control	Difficult	Easy
Resolution	Excellent	Comparable
Measurement	Instantaneous	Continuous
Mass production	Difficult	Easy
Cost	Very high	Fair

technique used to analyze gas mixtures. It is used to separate and identify chemical compounds from a mixture. However, multi-sensor devices allow on a quick and in a easy way to detect and determine the intensifying odorogenic gases in a near real time as well as substances lacking a perceptible odor (i.e., carbon dioxide and water vapor) [28–30].

2 Experimental

2.1 Analytical methods

The composition and analysis of biogas were carried out using a gas chromatograph (PerkinElmer AutoSystem XL) with a Porapak Q column (100–120 mesh 6.5 m × 1/8, pressure 200 kPa) and an oven temperature of 60 °C. The studies were carried using a thermo-conductivity detector (TCD, temperature 100 °C). Nitrogen with a flow of 30 mL/min was used as the carrier gas. The volume of the analyzed sample was 0.2 mL. During the analysis (15 min), TurboChrom software was used.

2.2 Dark fermentation

Dark fermentation was carried out with the use of wastewater mixed sludge (municipal wastewater treatment plant, Saur Neptun Gdańsk, Poland) after Faloye procedure with respect to distilled glycerin as the sole carbon source. Faloye procedure allowed to destroy non-spherical microorganisms [1, 2]. Dark fermentation was carried in triplicate in sterile 1200 mL glass bioreactors with a working volume of 1000 mL fermentation broth and under regulated pH conditions as described in the previous study [26, 31, 32]. The initial fermentation broth was composed of 900 mL of 20.0 g/L solution of Buffered Peptone Water (Biomaxima Gdańsk, Poland) and 5.5 g/L distilled glycerin as a sole carbon source. Control (negative) was carried in 20.0 g/L solutions of Buffered Peptone Water (Biomaxima Gdańsk, Poland) without glycerin and glucose control with Thioglycollate (Biomaxima Gdańsk, Poland) with the addition of 5.5 g/L of glucose. In each flask, 100 mL of Faloye-pre-treated inoculum was introduced to the broth at 37 °C (Table 2). The pH of fermentation broth was adjusted to 7.00 with 1 M NaOH. Before inoculation, anaerobic conditions were created by purging the reactors with sterile nitrogen (Linde, purity 99.98%) for 60 min. Operational set-points were set at 37 °C and 320 RPM (rotations/min) for temperature and agitation, respectively [26]. The composition of fermentation broths is presented in Table 2.

3 Results and discussion

Anaerobic digestion is a multi-step process carried out by consortia of highly diversified microorganisms and requires strictly anaerobic conditions. Such conditions enable the transformation of organic matter into carbon dioxide and methane, if methanogenesis is inactive. In the first stage of AD, organic matter, i.e., glycerin, is hydrolyzed; then, in the second stage, it is converted via fermentative bacteria to a mixture of minor products. In the third stage, acetogenic bacteria convert minor products to acetate, CO_2 and H_2. Consequently, as the terminal phase of the culture occurs, methanogenesis takes place [33]. Different microbial populations have specific optimum working conditions and are inhibited by several process parameters such as pH, temperature, alkalinity, concentration of free ammonia, hydrogen, sodium, potassium, volatile fatty acids (abr.VFA) or heavy metals.

The changes in the composition of gas formed during dark fermentation on diversified feed material are

Table 2 Composition of tested fermentation broths

Components	Fermentation broth		
	Glycerin broth	Glucose control	Negative control
Buffered Peptone Water 900 mL	20.0 g/L	–	20.0 g/L
Thioglycollate broth alternative	–	29.0 g/L	–
Glucose	0.5 g/L	5.5 g/L	0.5 g/L
Glycerin	5.5 g/L	–	–
Faloye-pre-treated inoculum	100 mL	100 mL	100 mL
Total volume	1000 mL		

presented in Fig. 2. During the experiment, all mentioned stages could be observed. When glucose was used as a sole carbon source (glucose control), no induction time concerning dark fermentation was observed. High concentrations of hydrogen were detected after 20 h of culture. The production of hydrogen lasted 96 h, after which the termination could be observed, as the hydrogen concentration dropped. In a similar broth, however, with a relatively lower glucose content (negative control), a small production of hydrogen was observed and methane was not detected. The course of dark fermentation for glycerin as a sole carbon source revealed an induction time. After 20 h of dark fermentation, the initiation phase passed to logarithmic growth phase. Hydrogen was generated till ca. 75 h of culture. In ca. 75 h of the culture, the hydrogen's terminal phase occurred and methanogens started to produce methane. The concentrations of methane obtained from the culture were even higher than the ones obtained for hydrogen. The authors expected to detect other gases, i.e., H_2S; however, its concentration was lower than the limits of detection in the used GC; therefore, a need to search for alternative gas composition determination has occurred. As the hydrogen productivity is concerned, it is crucial to determine the moment, when the hydrogen concentration drops and CH_4 and H_2S production occurs. The authors have placed a red line in the time point, for which the methane concentration starts to increase. From that moment, the produced gas stream needs to be separated, in order to keep a high purity of previously formed hydrogen. Unfortunately, the applied GC technique did not allow to determine the H_2S concentration, as its level was under the limit of detection (abr. LOD). The same situation has taken place for other fermentation gases, i.e., ammonia, carbon monoxide and oxygen. In other studies,

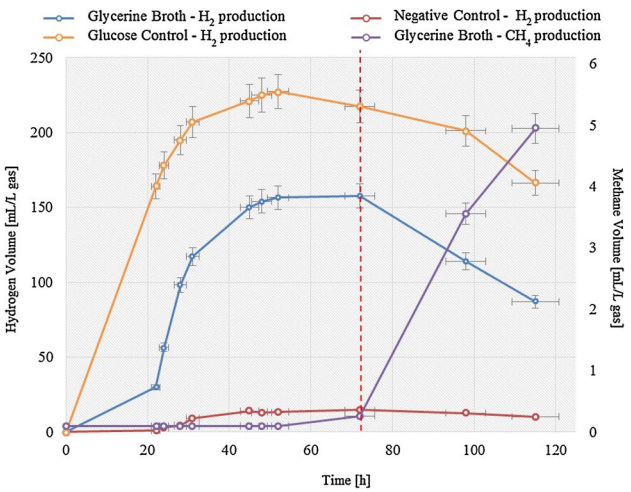

Fig. 2 Changes in gas composition occurring during dark fermentation with respect to hydrogen and methane

similar hydrogen productivity during dark fermentation was observed [34–36]. However, the data in the literature are very hard to compare, as they are normalized and often received in a diversified broths, volumes and with the application of varied process parameters, i.e., pH, temperature, agitation of even the type of wastewater sludge.

A delay in the GC analysis results may cause a delay in the hydrogen and methane streams separation. Therefore, the authors conducted that in order to carry out further tests, a review of commercially available gas sensors for the purposes of dark fermentation course analysis and gas composition determination is required.

On the basis of described research, the authors decided that further tests on the composition of fermentative gaseous products require alternative methods, i.e., gas sensors. Gas composition may be carried using a MOS type sensor, with CuO [37], which meets the criteria for typical fermentation gas measurements (Fig. 3). The sensor is selective for H_2S concentration, but also has a relatively good response to other gases potentially contained in the tested mixture. Therefore, a research on sensors used for fermentation control needs to be carried. The criteria of selection should include the selectivity not only for the hydrogen, hydrogen sulfide or methane, but also the sensitivity to the response of other gases contained in the mixture—ammonia, carbon dioxide and oxygen.

Examples of commercially available gas sensors, that might be applicable for the gases obtained via dark fermentation, are presented in Table 2. Sensors that are commercially available can be obtained from companies such as Duran Electronica and Figaro. Tables 3 and 4 show the examples of gas sensors and chromatographic methods with and their technical specifications, respectively. After analyzing the concentration ranges in which the sensors operate, it can be confirmed that readily available gas sensors meet the requirements for monitoring the dark fermentation process. However, as conducted during the fermentation, gas chromatography allows us to control only gases such as hydrogen, carbon dioxide and methane.

Comparison of the possibilities of detection concerning interesting fermentation gaseous products defined for both gas sensors (Table 3) and gas chromatography (Table 4) reveals that it was not possible to detect H_2S and NH_3 using gas chromatography. However, it is possible to detect mentioned gases using sensor matrixes. The literature reports very low concentrations of H_2S and NH_3 in the gaseous products [43–45]. Therefore, the limits of detection on the level 0–300 ppm for H_2S and 0–100 ppm for NH_3 may be satisfactory for the control purposes of dark fermentation. After analyzing the concentration ranges in which the sensors operate, it can be confirmed that readily available gas sensors meet the requirements for monitoring the dark fermentation process. On the other hand,

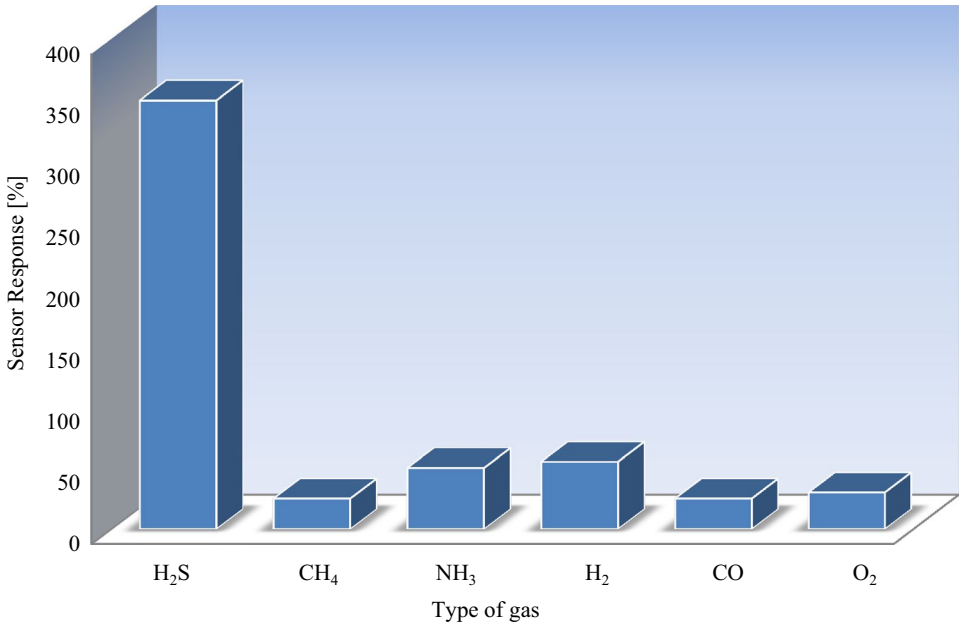

Fig. 3 Sensor response obtained for the CuO: 1 ppm H_2S and 100 ppm CH_4, NH_3, H_2, CO, O_2 according to [37, 38]

Table 3 Examples of commercially available gas sensors

Producer	Duran Electronica					Figaro
	SONDELTOX		SSQNRSNH3LI	SIRYRSCO2rLI	SSQNRH2SSrLI	TGS2611 MOS
References	[39]		[40]	[40]	[40]	[41]
Gas type	H_2S	H_2	NH_3	CO_2	H_2S	CH_4
Technical characteristics						
Measurement range (ppm)	0–300	0–200	0–100	0–20.000	0–100	500–10.000
Temperature range (°C)	− 20 °C to + 50 °C		− 10 °C to + 50 °C			–
Pressure range	Atm ± 10%		80–110 kPa			–
Time of response (s)	T90 < 35	T90 < 30	T90 < 30	T90 < 15	T90 < 20	–

gas chromatography did not detect H_2S or NH_3, so it only allows to control gases such as hydrogen, carbon dioxide and methane. The presence of other mentioned products needs to be confirmed in further research.

4 Conclusions

Complexed matrix of gaseous components may be formed and revealed during the dark fermentation process. The authors confirmed the presence of hydrogen, carbon dioxide, methane and oxygen during the process. Hydrogen was mainly generated in the initial, lag and log phase of the culture and methane in the late logarithmic death phase of the culture, only when glycerin was used a sole carbon source. However, other fermentation gaseous products' presence was not confirmed, as their concentration was under the limits of detection. The time point characterizing the moment when the methane production starts delivers some difficulties, as the gas chromatography delivers a slight delay regarding the results obtaining, as it is not a continuous method. As this time point is correlated with the appearance of CH_4 and H_2S, which occurs, when the metabolic pathway of bacteria and *Archea* take place, it seems crucial to determine other gases, not detectable using gas chromatography in the occurring levels. Therefore, a revision regarding the application of matrices sensors was proposed, and the levels of gases able to be measured using both gas chromatography and matrices sensors were conducted. The criteria of matrix sensors' selection should include the selectivity not only for the hydrogen, hydrogen sulfide or methane, but also the sensitivity to the response of other gases contained in

Table 4 Examples of gas chromatography methods for gas analysis

Producer	Shimadzu				
	GC/MS system (GCMS-QP2010 Plus) equipped with a CP-PoraPLOT Q-HT column				
Reference	[42]				
Gas type	H_2S	NH_3	H_2	CO_2	CH_4
Technical characteristics					
Limit of detection (LOD) (ppm)	n.d.	n.d.	335.9	5.1	3.3
Injection volume	200 µL				
Temperature	100 °C				
Head pressure	38.0 kPa				
Producer	PerkinElmer AutoSystem XL GC/FID/TCD equipped with a Porapak Q column				
Reference	This study				
Gas type	H_2S	NH_3	H_2	CO_2	CH_4
Technical characteristics					
Limit of detection (LOD) (ppm)	n.d.	n.d.	120	1500	700
Injection volume	200 µL				
Temperature oven/TCD	60 °C/100 °C				
Head pressure	200 kPa				

the mixture—ammonium, carbon dioxide and oxygen. A comprehensive combination of commercially available sensors and their applicability for the purposes of dark fermentation course analysis was presented on the basis of the levels of gas concentrations in the generated gas mixture. The authors conducted that the multi-sensor matrices may be a good alternative solution for fermentation gas measurement, especially when it is possible to apply them in a continuous matter. In addition, hydrogen sulfide and ammonia concentrations can be determined using gas sensors, which were under the limits of detection for gas chromatography. The application of sensor matrices for the dark fermentation course analysis needs to become a future step for the gas analysis and streams separation method development.

Author contributions ES and KK conceived, designed and carried the experiments. ES, KK, JG wrote the paper.

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Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; and in the decision to publish the results.

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