

Current State, Challenges and Perspectives of Biological Production of Hydrogen in Dark Fermentation Process in Poland

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ABSTRACT

The increasing demand for electrical energy and environmental concerns associated with conventional means of its generation drive the interest in alternative fuels. Biohydrogen, widely considered as fuel of the future, is one of such alternatives. To date, research results suggest that biological routes are the most promising for hydrogen production, especially dark (hydrogen) fermentation. Hydrogen fermentation can be performed with agricultural and food processing wastes as substrates. In this paper the most important factors influencing dark fermentation are reviewed and analyzed. These are: pH, partial pressure, temperature, and retention time. The biohydrogen generation efficiency is also presented with respect to different substrates. It should be also pointed out that many factors are still unknown; thus, the process requires conducting further research.

Keywords: renewable energy sources, biohydrogen, dark fermentation, wastes management, biogas plants

INTRODUCTION

The energy crisis and intensive degradation of the natural environment lead to the intensification of the search for harmless novel energy carriers. It is commonly acknowledged that the conventional processes of energy production are the cause of irreversible climate changes, global warming and faster depletion of natural resources [Ni et al. 2006]. The research data confirms that the greenhouse effect is a consequence of carbon dioxide emission from the use of fossil fuels [Budzianowski 2011]. Therefore, the search for new technologies of energy generation from alternative energy sources is necessary.

During the last decades, studies focused primarily on using biomass (in direct combustion), liquid biofuels (in esterification and transesterification) and methane (in anaerobic digestion process (AD) for the production of heat. Hydrogen is one of the alternative energy carriers considered

as an ecological biofuel of the future. It is characterized by high content of energy per unit of mass ($142 \text{ kJ}\cdot\text{g}^{-1}$) and its oxidation leads to the generation of water (steam) besides energy [Guo et al. 2010, Rahman et al. 2016]. It is possible to utilize hydrogen directly in internal combustion engines or fuel cells [Alves et al. 2013, Kotay et al. 2008]. It is commonly used as a reagent in the production of fertilizers, for oil refining and industrial ammonia synthesis. The issues that hinder the wide-scale application of hydrogen as a fuel are related to high costs of its production, and the technical problems associated with its storage and distribution. Commercially, it is produced in a steam reforming process from natural gas and oil and, to a lesser extent, through gasification of coal and water electrolysis [Balat 2008, Hassen Sellami and Loudiyi 2017]. However, as mentioned above, these processes are very energy-consuming and, moreover, they require fossil fuels. The production of hydrogen by biological

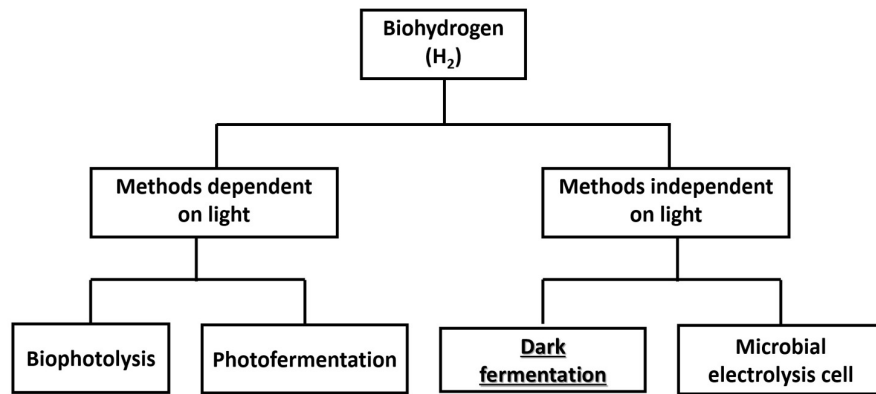


Fig. 1. Biological methods of hydrogen production [Ghimire et al. 2015]

means is thus promising as it does not require large quantities of energy (Figure 1).

The first observations regarding the hydrogen production by algae and bacteria were made over 100 years ago [Jackson and Ellms 1896]. A basic research in this area was carried out in 1929 by Strickland [Strickland 1929], research and development work began in the 1970. The biological processes of hydrogen production include direct biophotolysis of water carried out by algae, indirect biophotolysis of water using cyanobacteria, photofermentation with photosynthetic bacteria and dark fermentation (DF) conducted by anaerobic bacteria [Ghimire et al. 2015]. DF can become one of the important technologies of energy production from organic wastes such as complex agri-food industry by-products that can also be used in AD.

The aim of this paper was to review the current state of knowledge on the possibility of biological hydrogen production in the process of DF and the actual situation of the renewable energy market in Poland. The progress in the studies on the production of biohydrogen worldwide and the possibility of using substrates available in Poland in the process of DF were analyzed.

RENEWABLE ENERGY MARKET IN POLAND

The adoption of the climate and energy package by the countries of the European Union in March 2007 and the introduction of the Directive 2009/28/EC on the promotion of energy production from renewable sources were aimed at reducing the greenhouse gas emissions and the consumption of conventional fuels. As part of these activities, Poland committed itself that by 2020

the share of renewable energy sources (RES) in the final energy balance would increase to 15%, the energy efficiency to 20% and greenhouse gas emissions to the atmosphere would decrease by 20% compared to 1990. As a consequence of these actions, Parliament of the Republic of Poland adopted the Act on Renewable Energy Sources (AoRES) on February 20, 2015, which entered into force on May 4, 2015. The AoRES [2016] defines the Renewable Energy Source as renewable, non-fossil energy sources including wind energy, solar radiation energy, aerothermal energy, geothermal energy, hydrothermal energy, hydro energy, energy obtained from waves, currents and tides, as well as from biomass, biogas, agricultural biogas and from bioliquids. Table 1 presents the data on the share of RES in the total energy production for Poland and selected European Union countries (2004–2015) as well as the targets assumed for 2020.

Utilization of renewable energy in Poland has been growing systematically since the introduction of the supportive system. It should be noted that approx. 45% of the energy production from renewable sources – recognized by the Ministry of Economy as RES – is co-incineration of biomass with fossil fuels [Paska and Surma 2014]. According to the data of the Energy Regulatory Office (ERO), which regulates the Polish Energy Market, the total capacity of RES installations in Poland amounts to 8,440.459 MW. Table 2 presents the Energy Regulatory Office data on RES power capacity installed in Poland.

The largest share in the production of electrical energy from RES, excluding co-incineration, is assigned to wind farms (about 5,807,316 MW), which accounts for about 69% of the total energy production from RES. On the other hand, the lowest power capacity installed is for photovoltaic

Table 1. Percentage share of renewable energy in gross final energy consumption in European Union countries (in 2004–2015) [Eurostat Statistics Explained 2017]

	2004	2007	2008	2009	2010	2011	2012	2013	2014	2015	Target (2020)
EU – 28 countries	8.5	10.4	11.0	12.4	12.9	13.2	14.4	15.2	16.1	16.7	20
Poland	6.9	6.9	7.7	8.7	9.3	10.3	10.9	11.4	11.5	11.8	15
Austria	22.6	27.2	28.1	29.9	30.4	30.6	31.4	32.3	32.8	33.0	34
Belgium	1.9	3.1	3.6	4.7	5.7	6.3	7.2	7.5	8.0	7.9	13
Bulgaria	9.4	9.2	10.5	12.1	14.1	14.3	16.0	19.0	18.0	18.2	16
Croatia	23.5	22.2	22.0	23.6	25.1	25.4	26.8	28.0	27.9	29.0	20
Cyprus	3.1	4.0	5.1	5.6	6.0	6.0	6.8	8.1	8.9	9.4	13
Czech Republic	6.8	8.0	8.6	9.9	10.5	11.0	12.8	13.8	15.1	15.1	13
Denmark	14.9	17.8	18.6	20.0	22.1	23.5	25.7	27.4	29.3	30.8	30
Estonia	18.4	17.1	18.9	23.0	24.6	25.5	25.8	25.6	26.3	28.6	25
Finland	29.2	29.6	31.3	31.3	32.4	32.8	34.4	36.7	38.7	39.3	38
France	9.4	10.1	11.1	12.1	12.5	11.1	13.4	14.1	14.7	15.2	23
Germany	5.8	9.1	8.6	9.9	10.5	11.4	12.1	12.4	13.8	14.6	18
Greece	6.9	8.2	8.0	8.5	9.8	10.9	13.5	15.0	15.3	15.4	18
Hungary	4.4	5.9	6.5	8.0	12.8	14.0	15.5	16.2	14.6	14.5	13
Ireland	2.4	3.6	4.1	5.1	5.6	6.6	7.2	7.7	8.7	9.2	16
Italy	6.3	9.8	11.5	12.8	13.0	12.9	15.4	16.7	17.1	17.5	17
Latvia	32.8	29.6	29.8	34.3	30.4	33.5	35.7	37.1	38.7	37.6	40
Lithuania	17.2	16.5	17.8	19.8	19.6	19.9	21.4	22.7	23.6	25.8	23
Luxembourg	0.9	2.7	2.8	2.9	2.9	2.9	3.1	3.5	4.5	5.0	11
Malta	0.1	0.2	0.2	0.2	1.0	1.9	2.8	3.7	4.7	5.0	10
Netherlands	2.1	3.3	3.6	4.3	3.9	4.5	4.7	4.8	5.5	5.8	14
Portugal	19.2	21.9	23.0	24.4	24.2	24.6	24.6	25.7	27.0	28.0	31
Romania	16.3	18.3	20.5	22.7	23.4	21.4	22.8	23.9	24.8	24.8	24
Slovakia	6.4	7.8	7.7	9.4	9.1	10.3	10.4	10.1	11.7	12.9	14
Slovenia	16.1	15.6	15.0	20.1	20.4	20.3	20.8	22.4	21.5	22.0	25
Spain	8.3	9.7	10.8	13.0	13.8	13.2	14.3	15.3	16.1	16.2	20
Sweden	38.7	44.2	45.3	48.2	47.2	48.7	51.1	52.0	52.5	53.9	49
United Kingdom	1.1	1.8	2.7	3.3	3.7	4.2	4.6	5.7	7.1	8.2	15

Table 2. The power of RES installations in Poland [Energy Regulatory Office 2017]

Type of RES	Installed power [MW]							
	2010	2011	2012	2013	2014	2015	2016	2017
Biogas plants	82.884	103.487	131.247	162.241	188.549	212.497	233.967	235.373
Biomass power stations	356.190	409.680	820.700	986.873	1,008.245	1,122.670	1,281.065	1,362.030
Solar power stations	0.033	1.125	1.290	1.901	21.004	71.031	99.098	103.896
Wind power stations	1,180.272	1,616.361	2,496.748	3,389.541	3,833.832	4,582.036	5,807.416	5,848.671
Hydroelectric power station	937.044	951.390	966.103	970.128	977.007	981.799	993.995	988.377
AMOUNT	2,556.423	3,082.043	4,416.088	5,510.684	6,028.637	6,970.033	8,415.541	8,538.347

power plants (about 87.72 MW). However, it is worth noting that photovoltaic panels are mainly assembled as small domestic installations (producer). It can be assumed that in the near future there will be a dynamic development of this type of renewable energy installations due to the decreasing prices and increase in the efficiency of photovoltaic modules [Borenstain 2015, Griffin et

al. 2013]. It is also worth mentioning that every year, the number of installations that rely on RES is growing in Poland, and the highest increase was observed in 2016 (by approx. 1,445 MW). This is primarily due to the amendment to the Act on renewable energy sources introduced in June 22, 2016, which defined the direction of financial development of RES market in Poland (introduction

of the auction system) and concluded a period of uncertainty on the Polish RES market.

Financing of RES in Poland

Since October 10, 2005, the financing of renewable energy sources in Poland is based on the Tradable Green Certificates system (TGCs). As a consequence of the system, the producer of the energy obtained from wind, solar radiation, geothermal energy, waves, currents and tides and river falls, as well as from biomass gains property rights (the so-called Green Certificates) issued by the President of ERO. Each certificate corresponds to 1 MWh of the electricity generated. The property rights are traded on the Polish Power Exchange, which contributes to large fluctuations in prices, resulting from the current economic situation on the RES market (Figure 2).

In the recent years, the price of green certificates has fallen dramatically. Such losses of value resulted from the lack of legal regulations and the uncertainties regarding the future of financing the renewable energy in Poland. Currently, the price of a green certificate is the lowest since the launch of the Polish Power Exchange with the weighted average price as of June (in 2017) was 24.38 PLN/MWh. This situation means that many installations that rely on RES in Poland are on the verge of bankruptcy [Wędzik et al. 2017].

The introduction of the Renewable Energy Sources Act in 2015 was to improve the Polish market situation by changing the supportive system for RES installations. The legislator proposed an auction system. Pursuant to the act, the government of the Republic of Poland is to decide on the amount of renewable energy to be procured, and then announce auctions (separately for instal-

lations over 1 MWe and below 1 MWe), which will be won by the bidder who proposes the lowest price. The installations that win the auction are supported for 15 years. In addition, the RES Act introduced the concept of guaranteed feed-in-tariffs (FiT) for electricity producers having small, backyard installations, at guaranteed prices for a period of 15 years. The owners of the plants with a capacity of up to 3 kW were to receive a guarantee of energy sales at a price of approx. 0.75 PLN/kWh, whereas the 3–10 kW range at a price up to 0.70 PLN/kWh, depending on the RES technology. The number of micro-installations for which funding is provided was limited, and the tariff system was suspended after the total installed power capacity exceeded 800 MW.

However, on July 1, 2016, the last amendment to the AoRES in Poland came into force. This document introduced a new division of installations participating in auctions. These installations have been classified in the following groups:

1. installations using electric power in total, regardless of the source, greater than 3504 MWh/MW/year;
2. installations generating electrical energy partly from industrial and municipal waste of plant or animal origin, including the waste from waste treatment as well as water and wastewater treatment, in particular sewage sludge, in accordance with the provisions on waste in the scope of partial energy recovery from the thermal treatment of waste;
3. installations in which the CO₂ emission does not exceed 100 kg/MWh, with a utilization rate of electric power installed higher than 3504 MWh/MW/year;
4. members of the energy cluster;
5. members of the energy cooperative;

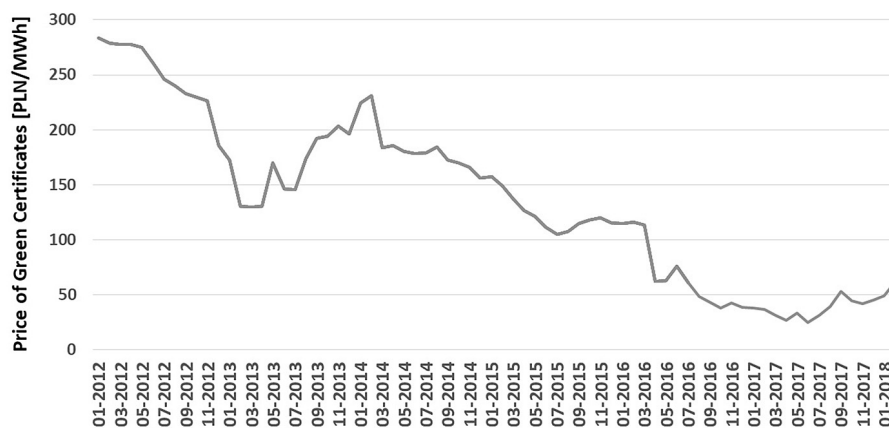


Fig. 2. Weighted average price of “green certificates” in 2012–2018 [Polish Power Exchange 2018]

6. installations using only agricultural biogas for generating electricity;
7. other installations.

Moreover, according to the law in force, RES installation owners can decide themselves whether they want to stay in the old Tradable Green Certificate system, or if they want to use the new auction system. In order to improve the financial situation of agricultural biogas plants operating on the basis of the old system, the Polish government introduced the blue certificate (PMOZE_BIO). This instrument is granted to the installations that have agricultural status and is a solution that has definitely improved the situation on the biogas market in Poland (Figure 3).

In May 2017, the price of the blue certificate increased to over PLN 400/MWh (Figure 3), which contributed to the increased interest in biogas production in Poland. However, in June this price went down to 369.57 PLN/MWh. In addition, the Polish government is working on another law amendment aimed at limiting the excessive increase in the price of certificates. Currently, there are 96 agricultural biogas plants operating in Poland, with a total installed power capacity of 101.093 MW [National Center for Agricultural Support 2018]. However, despite the introduction of a new renewable energy support system in Poland, the vast majority of investors remained in the old “green certificates” system.

POTENTIALS OF HYDROGEN PRODUCTION IN POLAND

The complicated situation in terms of supporting the financing of RES installations para-

doxically contributed to the development of new technologies in Poland. On the basis of the growing interest in renewable energy sources and the support of the Polish government for development of innovative technologies in the field of energy production, the development of the hydrogen production and distribution market is also expected. Energy-rich and green gas fuel produced from organic waste can contribute to the diversification of energy sources and increase the energy security of the country [Kazimierowicz 2014, Wiater and Horysz 2017].

Thus far, numerous research results on hydrogen production in the DF process have been presented in the scientific literature. However, it should be noted that glucose or other simple sugars were used as a substrates in a large part of these studies [Calli et al. 2008, Collet et al. 2004, Ghosh and Hallenbeck 2009, Kumar and Das 2000, Mizuno et al. 2000, Schröder et al. 1994, Van Niel et al. 2002]. Unfortunately, at an industrial scale, the use of such substrates is economically unjustified; therefore, the research on hydrogen production from composite substrates has the greatest significance for industrial installations. Such substrates include the organic waste from agri-food industry characterized by high energetic potential (Table 3). It is worth highlighting that the recent years have seen increasing interest in multi-directional use of these materials [White et al. 2013, Czekala 2018]. This interest has been in a large part motivated by the aim of limiting storage of organic materials in landfill sites that leads to their uncontrolled decomposition. The data reported by the European Commission shows that in 2010, more than 89 million Mg of food waste were generated in Europe, out of which almost 35 million Mg constituted the waste

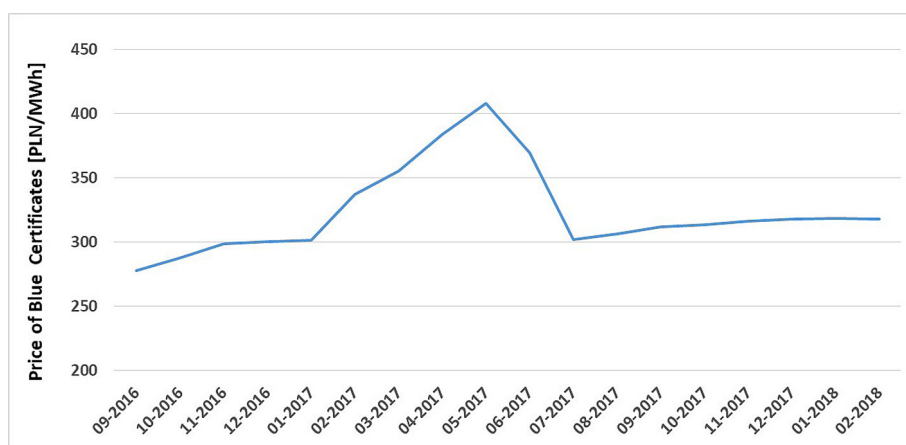


Fig. 3. Weighted average price of “blue certificates” in 2016–2018 [Polish Power Exchange 2018]

Table 3. Biohydrogen production yields of DF of agricultural waste.

Substrate	Biohydrogen yield (ml H ₂ /g VS)	Reactor operation mode	Temperature (°C)	Pretreatment	Reference
Cattle manure	65	Batch	52	90°C, 3 h	[Guo et al. 2010]
Cattle wastewater	53 ^a	Batch	45	–	[Tang et al. 2008]
Cheese whey	290 ^a	CSTR	35	NaHCO ₃ 20 g/L	[Venetsaneas et al. 2009]
Chicken skin	10	Batch	35	–	[Zhu et al. 2009]
Corn stover	49 ^a	Batch	35	220 °C 3 min	[Datar et al. 2007]
Corn stover	66 ^a	Batch	35	1.2% HCl + 200 °C 1 min	[Datar et al. 2007]
Corn straw	9	Batch	35	–	[Li and Chen 2007]
Corn straw	68 ^a	Batch	35	1.5 MPa 10 min	[Li and Chen 2007]
Cornstalk	3	Batch	36	–	[Zhang et al. 2007]
Cornstalk	57	Batch	36	0.5% NaOH	[Zhang et al. 2007]
Cornstalk	150	Batch	36	0.2% HCl boiled 30 min	[Zhang et al. 2007]
Cow feces and urine	18 ^a	Batch	75	–	[Yokoyama et al. 2007]
Cow feces and urine	29 ^a	Batch	60	–	[Yokoyama et al. 2007]
Cow feces and urine	0.7 ^a	Batch	37	–	[Yokoyama et al. 2007]
Dairy manure	18	Batch	36	0.2% HCl boiled 30 min	[Xing et al. 2010]
Dairy manure	14	Batch	36	0.2% NaOH boiled 30 min	[Xing et al. 2010]
Dairy manure	14	Batch	36	Infrared radiation 2 h	[Xing et al. 2010]
Dairy solid cow waste	97	Batch	35	2.5% oxalic acid, 50 g/L dairy cow solid waste and boiled 30 min	[Chu and Wang 2017]
Food waste	196	Batch	36	160 °C 2 h	[Li et al. 2008]
Food waste	60 ^a	Batch	35	n.d.	[Kim et al. 2004]
Food waste	77	Batch	35	–	[Lay et al. 2005]
Food waste	125 ^a	CSTR	35	–	[Shin and Youn 2005]
Food waste	65	Semi-continuous rotating drum	40	–	[Wang and Zhao 2009]
Food waste	13	CSTR	20	–	[Karlsson et al. 2008]
Food waste	3	CSTR	37	–	[Karlsson et al. 2008]
Grass silage	6	Batch	35	–	[Karlsson et al. 2008]
Grass silage	16	Batch	70	–	[Karlsson et al. 2008]
Maize leaves	18	Batch	70	–	[Ivanova et al. 2009]
Maize leaves	42	Batch	70	130 °C 30 min	[Ivanova et al. 2009]
Pig slurry	4	CSTR	70	–	[Kotsopoulos 2009]
Swine liquid manure	209 ^a	Semi-continuously-fed fermenter	35	–	[Xing et al. 2010]
Wheat straw	1	Batch	36	–	[Fan et al. 2006]
Wheat straw	68	Batch	36	HCl 2% + microwave heating	[Fan et al. 2006]
Wheat straw	49 ^a	Batch	70	130 °C 30 min	[Ivanova et al. 2009]

^aCalculated from literature data

from the manufacturing sector [European Commission 2010]. Large amounts of organic waste are also produced in Poland, including about 6.5 million Mg of waste from food production, 2 million Mg of waste from household, 90 million Mg

of manure and slurry, and more than 10 million Mg of waste straw produced each year. These materials can be applied for the production of ecological gas fuels – methane and biohydrogen. The agri-food sector generates three distinguishable

types of waste: the wastes generated from direct agricultural production and post-harvest residues, animal production wastes (manure and slurry) and food waste [Guo et al. 2010].

Slurry and manure

Slurry, a mixture of animal feces and urine (mostly cattle or swine) and water from washing positions and watering, is one of the most common biogas substrates in Europe and Poland [Dach et al. 2014, Dach et al. 2016]. It is a side-product of non-bedding animal husbandry systems. Slurry is a natural fertilizer with a high content of nutrients in the forms that are easily available to plants. Its composition depends primarily on the degree of dilution with water, but also on the type of animals, age and the method of feeding. According to the available data, this material has N_{total} content of 1363 mg/L, P_{total} content of 255 mg/L and COD of 47,820 mg O_2 /L [Marszałek et al. 2014].

According to the data provided by the National Center for Agricultural Support (NCAS) [2017], approximately 598,807 and 774,997 Mg this material were used for AD, in 2015 and 2016, respectively. In the biogas plants built at cattle and swine farm, slurry is suitable for diluting solid substrates (consisting mainly of plant materials). The biogas yields of cattle and swine slurry are approximately 210 m³/Mg VS and 250 m³/Mg VS, respectively [KTBL 2009]. The results of research carried out by Yokoyama et al. [2007] and Kotsopoulos [2009] showed that these materials can also be considered as substrates for hydrogen fermentation.

Manure is another type of natural fertilizer used in AD. This material is a mixture of animal droppings with straw. As in the case of slurry, it is characterized by high fertilizing value. Its chemical composition depends primarily on the amount of spent litter and the species of animals, their way of feeding and health. This material can also serve as a substrate for the production of biohydrogen.

The study of Guo et al. [2010] showed that cattle manure allows obtaining maximum hydrogen efficiency at a level of 65 ml/g VS. However, its utilization for energy purposes in Poland is limited to the production of biogas and biomethane. In 2016, 86 144.669 Mg of this material were used in Polish agricultural biogas plants [National Center for Agricultural Support 2017].

It should also be added that animal droppings, and especially manure of pigs and poultry, are characterized by high nitrogen content [Angelidaki and Ahring 1994, Hansen et al. 1998], which can inhibit the fermentation process and hydrogen production [Hobson et al. 1974]. This makes using these substrates in mono-fermentation difficult [Fatina et al. 1988, Van Velsen 1979]. Using co-fermentation with lignocellulosic materials in the batch mixture can be a solution to this problem as it enables to obtain a suitable C/N ratio [Neshat et al. 2017].

Food waste

Production of large amount of food waste is one of the most important problems of the modern world (including in Poland). Scientific research shows that between 1/3 and 1/2 of the food produced worldwide is not consumed [Gustavsson et al. 2011]. This results in negative effects on the entire food supply chain. In addition, improper management of this type of waste may contribute to the deterioration of the natural environment. In Poland, over 47 million Mg of food are produced yearly, which makes approx. 172 kg of food per capita yearly. However, it should be kept in mind that about 14% of food is already wasted during the production phase [European Commission 2010]. Due to high heterogeneity, high water content and low calorific value, the use of food waste for direct energy production through combustion is difficult. Biological processing, such as fermentation and composting, were proposed as suitable means of the management of these materials [Cerdeira et al. 2018, Yasin et al., 2013]. The studies carried out so far have shown that food waste can have a dry matter content of 10 to 26% and a C/N ratio in the range of 14.7–36.4 [Thi et al. 2015]. However, it should be remembered that the manner of its collection and storage can significantly affect the content of inorganic and organic matter, which can reduce the efficiency of biological processes.

The production of biohydrogen, undergoing development for the last 15 years, can serve as an innovative method of biological processing. Numerous tests aimed at determining the efficiency of hydrogen generation from food waste have been carried out [Chu et al. 2012, Danko et al. 2008, De Gioannis et al. 2017, Yun et al. 2018]. The results show high hydrogen production potential that largely depends on the type of pre-treatment

of the inoculum [Yasin et al. 2013]. A large potential for biohydrogen production from food wastes can also be anticipated in Poland. Residues of fruits and vegetables are currently one of the most commonly used batch material by Polish investors in biogas plants. In 2016, 665,338.208 Mg of such substrates were used in Polish biogas plants, which accounted for approx. 20% of all materials used in the fermentation process. Specifically, 28,596.802 Mg of waste from food processing, 25,962.931 of residues from processing of fruits and vegetables, and 2,851.251 Mg of restaurant waste were utilized for AD in 2016 [National Center for Agricultural Support 2017]

Dairy industry waste

The waste from the dairy industry is another type of waste that significantly affects the environmental pollution. Production in dairy plants results in several types of technological waste and leachates, both in liquid and solid forms. Whey, a by-product of cheese production, is one of the most dangerous dairy wastes. It contains approx. 600 mg N/L, and its COD and BOD₅ levels are 27–60 g/L and 50–102 g/L, respectively [Carvalho et al. 2013]. Two types of whey are formed as a result of precipitation of casein in the production process – acid and sweet whey. The acid whey (pH <5) is produced after the fermentation process or after the addition of organic or mineral acids. On the other hand, the sweet whey (pH = 6–7) is obtained as a result of the addition of proteolytic enzymes [Carvalho et al. 2013, Panesar et al. 2007]. The dry matter of whey obtained from cow milk contains about 70–80% of lactose, about 9% of proteins and about 8–20% of minerals and other trace components [Daufin et al. 1998].

The second type of liquid waste in dairy plants is buttermilk. However, it may be used in the production of food buttermilk, which is why it is not considered a pollutant. Moreover, technological wastewater is generated during dairy production, containing high loads of organic matter. The most common way of its treatment utilizes traditional wastewater treatment plants that use activated sludge or sequencing batch reactors (SBR) [Wichern et al. 2008, Wu et al. 2008]. Such treatment results in the formation of sediments. The wastes from the dairy industry do not contain dangerous substances or heavy metals but are characterized by high organic load, which can reach approx. 15 g/L COD [Carvalho et al. 2013,

González Siso 1996]. This creates difficulties for typical wastewater treatment plants. Therefore, AD [Mata-Alvarez et al. 2000, Naik et al. 2010, Saxena and Adhikari 2009, Ward et al. 2008] or DF [Ghimire et al. 2015] may be the most appropriate means of their safe utilization.

The data of NCAS shows that in 2015, approximately 47,817.242 Mg of waste from the dairy industry were supplied to the Polish agricultural biogas plants. In 2016, the amount increased to 89.1414.969 Mg as a result of the development of the renewable energy sector. The popularity of dairy wastes in biogas generation is also a consequence of the high yields obtained using this substrate (253.85 Nm³ CH₄/Mg VS for whey) [Kozłowski et al. 2016]. The waste from dairy industry can be used in the production of biohydrogen. Venetsaneas et al. [2009] reported obtaining about 290 ml H₂/g VS in DF.

Maize silage

Maize silage, while not classified as a waste of agricultural industry, has become a staple in fermentation. It is one of the most commonly used substrates in biogas plants in Central and Eastern Europe [Dach et al. 2014, Hermann et al. 2015]. Its popularity is a result of high yield of biogas and methane reaching approximately 6050 – 6750 m³/ha [Piwowar et al. 2016]. Moreover, monofermentation of this substrate does not pose serious problems at the industrial scale. High demand for maize silage as biogas substrate is reflected in data. In 2016, the maize silage usage in biogas production amounted to 439,135.422 Mg in Poland. In Germany, this substrate constitutes 70% of all substrates used for energy generation [Multerer 2014]. The demand for corn silage has also driven an increase in its price, which is 25–35 Euro/Mg.

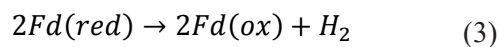
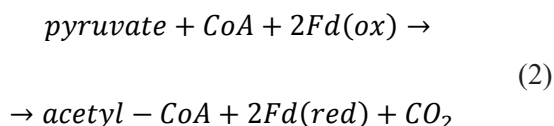
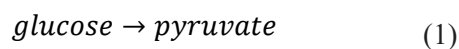
Corn silage is a substrate that does not require complicated treatment prior to storage, which is an additional advantage. It is common to ferment corn in bunker silos covered with plastic foil in order to reduce the oxygen supply. Following silaging (after approximately 4–6 weeks) the substrate can be directly fed into a biogas installation [Murphy et al. 2011]. During silaging under anoxic conditions, lactic acid bacteria convert carbohydrates into lactic acid which serves as a natural preservative. Besides lactic acid, acetic acid and other volatile fatty acids (propionic, formic, caproic, valeric)

and alcohols (ethanol, methanol, propanol) are formed. Care should be taken to avoid excessive oxygen diffusion, as it may result in formation of butyric acid which negatively impacts methane fermentation [Hermann et al. 2015]

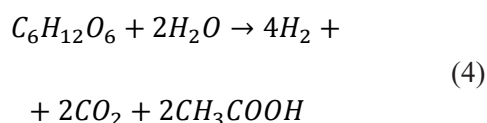
The data obtained from studies in continuous system indicates that corn silage fermentation yields 53.8 NI H₂/VS [Benito Martin et al. 2017]. However, application of this substrate to DF, may pose problems because of significant content of lignin and cellulose.

BIOHYDROGEN PRODUCTION IN DARK FERMENTATION PROCESS

During DF, metabolic pathways, known well from the studies on methane fermentation and hydrogenase enzyme, are utilized. First, glucose is metabolized to pyruvate (Eq. (1)) which is then oxidized in the second step to acetyl coenzyme A with simultaneous reduction of ferredoxin (Fd) (Eq. (2)). In the third step, ferredoxin undergoes oxidation catalyzed by hydrogenase with the resulting release of molecular hydrogen (Eq. (3)) [Adams and Stiefel 1998].

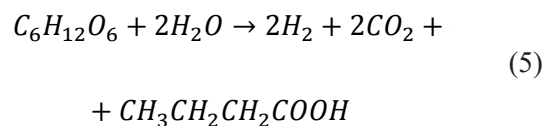


Carbohydrates, proteins and fats are transformed into volatile fatty acids. Theoretically, one mole of glucose yields 4 moles of molecular hydrogen, 2 moles of carbon dioxide and two moles of acetate (Eq. (4)).



In reality, however, the obtained yields range between 1 to 2.7 moles of molecular hydrogen that form 1 mole of glucose (Eq. (5)) [De Gioan-

nis et al. 2017]. The deviation from the theoretical yield is a result of production of butyrate.



Because of the partly shared metabolic pathways between methane and hydrogen production, a high yield hydrogen production process demands inhibition of acetogenesis and methanogenesis (Fig. 4) [Adams and Stiefel 1998]. Initial heat treatment of the culture may be applied to stop methanogens (80–104°C for 15–120 min) [Kraemer and Bagley 2007, Nath and Das 2003]. Methanogenic bacteria, unable to form spores, do not survive extreme temperatures, as opposed to the sporulating hydrogen producers. Applying short hydraulic retention times (HRT) and treatment of the substrate with acid are other effective methods of inhibiting methanogenesis and increasing hydrogen yield [Guo et al. 2010].

Production of hydrogen during DF is also dependent on the type of substrate, its concentration in the bioreactor and the microorganisms introduced with the inoculums. The research data indicates that utilizing mixed cultures from natural sources (e.g. compost, anaerobic fermentation) yields the best results. It is also possible to utilize non-sterilized substrates because of such approach [Hawkes et al. 2002].

ENVIRONMENTAL PARAMETERS OF DARK FERMENTATION

Temperature

Hydrogen generation during fermentation is dependent on temperature, among other factors. According to the van't Hoff equation, the rate of a chemical reaction increases along with the temperature. Fermentation, however, is catalyzed by the microorganisms that are prone to activity loss at temperatures that deviate from their optimum. Most studies on biohydrogen fermentation have been conducted at mesophilic temperatures (30–40°C) [Wang and Zhao 2009, Dong et al. 2009, Hong and Haiyun 2010, Lee and Chung 2010, Zong et al. 2009]. The results showed increasing hydrogen production up to 40°C and inhibition of the process at 45°C [Kim et al. 2008].

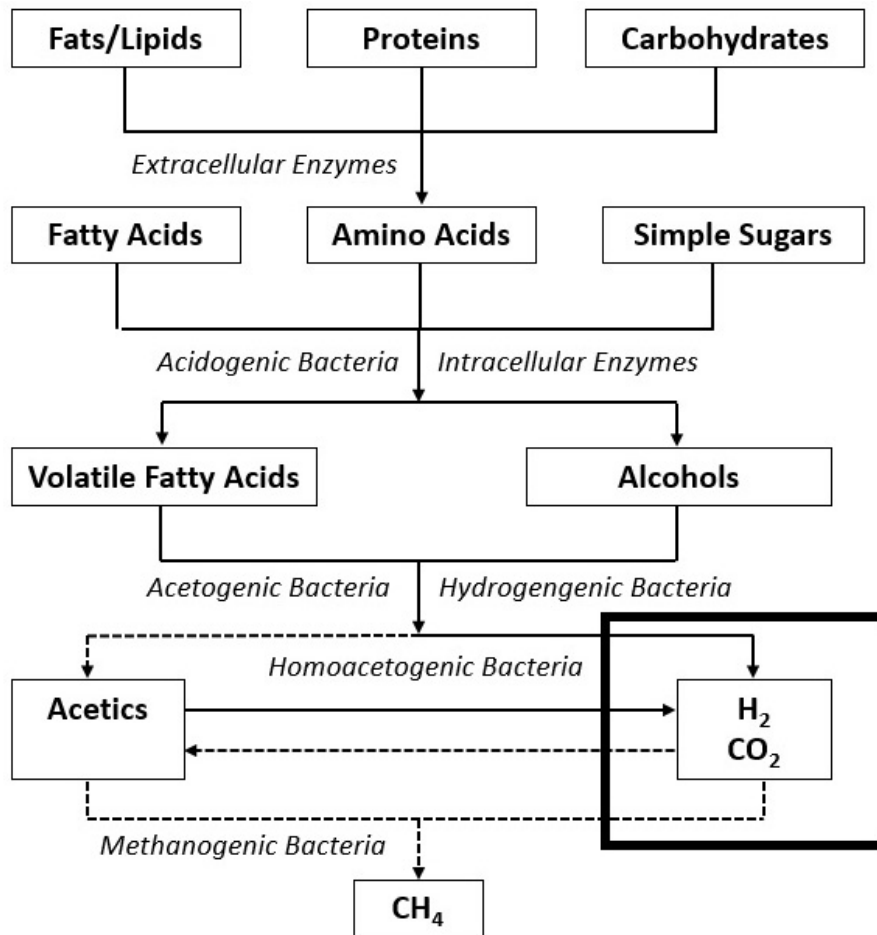


Fig. 4. Scheme of AD [Mao et al. 2015].

DF under thermophilic conditions has also been investigated. Elevated temperature resulted in the increased enzymatic activity (hydrogenases) and inhibition of microorganisms responsible for lactic acid formation [Lay et al. 1999, Oh et al. 2004, Valdez-Vazquez et al. 2005].

pH

Maintenance of proper pH value throughout the process of DF is crucial for obtaining hydrogen with a high yield. This parameter influences the hydrogenase activity which is responsible for the oxidation of ferredoxin with the release of molecular hydrogen. The research data indicates that low pH values may lead to the inhibition of this enzyme [Khanal et al. 2004, Nazlina et al. 2011].

The balance between metabolic pathways is modulated by pH which leads to different profiles of formed metabolites. At pH in the range of 4.5–6.0, mostly acetate and butyrate are released, at neutral and basic pH values, the generation of ethanol and propionate predominates [Guo et al.

2010]. Suppression of methanogenesis is an important effect of decreased pH.

The optimum pH for hydrogen fermentation is dependent mainly on the substrate used. The pH of 5.5 is optimal for the wastes generated during food processing [Shin and Youn 2005]. Substrates of a more complex nature (corn or wheat straw for example) showed better hydrogen yields when fermented at pH of 7.0–7.5 [Li and Chen 2007, Karlsson et al. 2008, Fan et al. 2006]. The optimum pH values for fermentation of various agricultural and industrial wastes with mixed bacterial cultures are summarized in Table 4.

Biohydrogen partial pressure

Maintaining low partial pressure of hydrogen in the bioreactor is crucial in order to achieve high effectiveness of the hydrogen production process in DF. Awareness of the influence of temperature on this parameter is important [Levin et al. 2004]. There are a few approaches that allow to limit the concentration of dissolved hydrogen. The data obtained thus far, indicated that increasing the

Table 4. Optimal value of pH in DF for different substrates

Substrates	pH range	Optimal pH	Reference
Food waste	5.0 – 6.0	5.5	[Shin and Youn 2005]
Grass silage	4.0; 5.0; 6.0	6.0	[Karlsson et al. 2008]
Maize straw	4.0 – 8.0	7.0–7.5	[Li and Chen 2007]
Wheat straw	4.0 – 9.0	7.0	[Fan et al. 2006]

rate of the stirrer in the fermentation tank may serve as the simplest method [Chou et al. 2008]. Sparging with different gas (nitrogen, argon, carbon dioxide or methane) may help remove the dissolved hydrogen. Introduction of sparging, however, results in dilution of hydrogen in the produced biogas and, what is even more important, its application at industrial scale would have a negative impact on the financial balance of the plant. Application of membrane techniques for limiting hydrogen partial pressure in the tank has also been proposed [Liang et al. 2002, Nielsen et al. 2001, Toplyakov et al. 2002].

CURRENT STATE, LIMITATIONS AND FUTURE RESEARCH

Currently, identification of economical substrates for future implementation in industrial-scale DF processes is one of the most important tasks. The biomass obtained, for example, from the first stages of photofermentation, energetic plants or organic waste from industry may be used for fermentative processes. These may be considered interesting substrates for biohydrogen production, yet their application still requires research. It should be pointed out that the suitability of various substrates for biohydrogen production is difficult to assess because studies show different yields even for the same type of feed. It is a result of applying different microorganisms and the variability of the substrates themselves, and the effect of these factors on the metabolic pathways that are active during fermentation that in turn affect the hydrogen production [Monlau et al. 2013]. Moreover, the conditions under which various studies are conducted differ significantly, as there are no standard methods concerning substrate pretreatment and fermentation parameters.

Significant progress has been made towards understanding the biochemistry of biohydrogen generation, including molecular and biochemical characterization of the enzymes involved, description of pathways responsible for supply of reducing equivalents and physiology of various microorganisms known to produce H₂ [Hallenbeck 2001]. Moreover, genetic manipulation shows a potential to improve the process through redirection of the flow of electrons in the microbial metabolism towards hydrogen generation [Keasling et al. 1998]

All the aspects mentioned above concern the hydrogen generation from any substrate, and should be taken into account in research plans concentrated on the bioconversion of residual agricultural or processing biomass to biohydrogen in DF.

CONCLUSIONS

The DF process can be utilized for the production of high-energy and green gas fuel (hydrogen) on an industrial scale all over the world. The substrates used in the described process may come from the agro-food waste, which would significantly reduce their uncontrolled decomposition in the environment. Food waste, straw, grass silage are a materials characterized by a high potential for hydrogen production. However, it should be remembered that the gas production efficiency is significantly affected by the composition of the substrate added to the fermentation reactor. Moreover, special attention should be paid to the basic environmental parameters (including temperature, pH and hydrogen molecular pressure) which ought to be controlled and regulated at appropriate levels in order to enable efficient and effective fuel production. However, the impact of many factors on the hydrogen fermentation process is still unknown. Therefore, further research on biohydrogen production is necessary.

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