# PRODUCTION OF HYDROGEN AND ELECTRICITY IN A MICROBIAL FUEL CELL

**Nizhnyi D.A.**
**Igor Sikorsky Kyiv Polytechnic Institute, nizhnyi.danyil@lll.kpi.ua**

**Introduction**. Hydrogen is a promising renewable energy source that can reduce greenhouse gas emissions and dependence on fossil fuels. However, current methods of hydrogen production using non-renewable energy sources have limitations such as high energy requirements, high production costs and low efficiency. The search for alternative renewable raw materials and ways of extracting hydrogen and electricity from them is urgent. The enzymatic method has a low yield of hydrogen (up to 4 mol of $H_2$/mol of glucose), but with the combined use of the two processes in a microbial fuel cell (MFC), it is possible to obtain an ecologically clean resource - hydrogen and simultaneously obtain electricity or increase the yield of hydrogen. The aim is to analyze methods of increasing the efficiency of MFC for the production of electricity and hydrogen from waste.

The process of dark fermentation (DF) with the production of biogas, which contains hydrogen and not methane, is a promising method for the production of hydrogen from organic waste. But this process has limitations caused by the transition of the process to methanogenesis and the use of hydrogen by consumers, which the association of microorganisms contains. The technology of microbial fuel cells allows to convert organic compounds into electricity with the help of electroactive bacteria.

The task is to consider approaches to increase the generated power and hydrogen yield in MFC, namely:

- approaches with and without supplying additional energy to the MFC;
- a comparison of the use of monoculture and microbial association;
- selection of the optimal parameters to increase the yield of hydrogen in MFC.

Most of the substrate during fermentation is converted into carboxylic acids (CC), such as volatile fatty acids (VFA) and lactic acid, which limits the output of $H_2$. Integrating DF with a microbial fuel cell (MFC) or microbial electrolysis cell (MEC) can further convert CC into bioenergy such as $CH_4$, $H_2$ and electricity. The simultaneous application of DF and MFC (sDFMFC) in one reactor can be a promising strategy for significant cost savings and obtaining energy and energy carriers. [4].

**Materials and methods.** For this thesis, a systematic review and meta-analysis were conducted to analyze published scientific articles on hydrogen and electricity production in microbial fuel cells. The literature research involved a comprehensive search of multiple databases, systematic screening and selection of articles based on predefined criteria, quality assessment of included studies, standardized data extraction, and rigorous statistical analysis.

**Results and discussion. I. Enzymatic processes of hydrogen production without light**. Fermentation is a method of biohydrogen production by various types of microorganisms, such as facultative and obligate anaerobes. The process takes place in the absence of light. The efficiency of biohydrogen generation during dark fermentation is influenced by biomass pretreatment methods, the sugar content of the substrate, and the microorganisms contained in the association. The theoretical yield of hydrogen can be estimated based on the metabolic pathway of microorganisms and the initial concentration of sugar in the fermentation medium. The three (1-3) thermodynamically favorable dark fermentation metabolic pathways for the conversion of organic substrates to biohydrogen are:

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

$$7C_6H_{12}O_6 + 6H_2O \rightarrow 24H_2 + 6CH_3CH_2COOH + 18CO_2 \quad (2)$$

$$CH_3COOH \rightarrow CH_3CH_2OH + H_2 \quad (3)$$

Dark fermentation produces a mixed gas containing $H_2$ and $CO_2$ with other impurities such as CO and $H_2S$ depending on the type of microorganisms and the substrate. No microorganism or consortium has been reported to result in complete substrate bioconversion during dark fermentation to hydrogen due to a positive Gibbs free energy value. The highest theoretical yields of biohydrogen are obtained for the formation of acetate as the final product. A mixture of acetic and butyric acids as final products can fetch maximum hydrogen generation. Microorganisms used in hydrogen fermentation are Clostridia, *Enterobacter, Escherichia coli, Citrobacter, Alcaligenes, Bacillus, Lactobacillus,* Micrococcaceae, Peptococcaceae, Vibrionaceae and Veillonellaceae. The production of biohydrogen increases using thermophilic conditions compared to mesophilic ones. The maximum hydrogen yield of 4 moles per mole of glucose is found under extremely thermophilic conditions (70 °C) by the thermophilic bacteria. On the other hand, hydrogen production decreases to 1 mol under mesophilic conditions and less than 2 moles per mole of glucose in thermophilic conditions [1].

Fermentation byproducts can be used to increase the commercial value of biohydrogen. Parameters affecting hydrogen production during fermentation include temperature, pH, hydraulic retention time, volatile fatty acid content, $H_2/CO_2$ partial pressure, and inorganic content. The high-temperature range during fermentation limits the growth of pathogenic bacteria, and the pH level has the potential to increase biohydrogen production [1].

In [2], it was shown that pH is the most important factor for increasing $H_2$ production, since at low values, the process of methanogenesis is inhibited. Artificial Intelligence (AI) techniques such as Artificial Neural Network (ANN) and Support Vector Machine (SVM) were used to analyze the results. SVM is found to be better than ANN and response surface methodology (RSM) in predicting the output of $H_2$. Genetic algorithm (GA) and particle swarm optimization (PSO) were used to determine the optimal process parameters, with PSO being faster than GA. Under the optimized conditions of pH 6.75, glucose-degrading organic compound (GDOC) concentration 16.16 g/L and temperature 37.55 °C determined by the SVM-GA and SVM-PSO models, the maximum $H_2$ yield of 8.28 mol H 2 $kg^{-1}$ COD removed was achieved, which was 2.1 times better compared to non-optimized parameters [2].

**II. Microbial fuel cells.** A microbial fuel cell (MFC) is a bioelectrochemical system that uses microorganisms to convert chemical energy stored in organic matter into electrical energy through substrate oxidation. Anaerobic bacteria at the anode oxidize the organic substrate, generating protons and electrons that are transferred to the cathode, producing water and electricity. MFCs were modified in such a way that 2 processes took place at the same time – obtaining hydrogen in the anode chamber and at the cathode (MEC), that is, combining electrochemistry with bacterial metabolism to produce hydrogen. To obtain hydrogen at the cathode, an external voltage is applied, which allows hydrogen to be obtained at the cathode. The applied voltage must be greater than the equilibrium voltage generated in the MFC. Under such conditions, it is possible to obtain up to 11 mol of $H_2$ per mol of glucose.

Electrode materials impact the formation of hydrogen at the cathode. The carbon-based cathodes used, such as Mo2C/N-rGO nanocomposites, were found to be the most efficient, while photocathodes coated with light-sensitive materials also performed well. Different types of cathodes, including stainless steel mesh, foamed nickel, and Ni-Co-P electrodeposited on SS316, were tested for effectiveness, with the latter being found to be the most cost-effective. SSM/PANI/graphene electrodes have also been found to show promising results in hydrogen production at a slightly lower cost than platinum electrodes [3].

Biological factors in MFCs and MECs are important. In the MEC, bacteria are common with various phyla and classes including Proteobacteria, Bacteriodetes and Clostridia. Pseudomonadaceae, Comamonadaceae, and Geobacteraceae are electroactive microbes that produce hydrogen. In MFC, the dominant classes are Proteobacteria and Bacteroidetes. *Lactobacillus* sp., *Propionibacterium* sp. and *Clostridium* sp. were found to increase the yield of biohydrogen. *Desulfovibrio*, *Butyricicoccus*, *Petrimonas* and *Propionivibrio* were the highest proportion of bacteria in MFC [3].

The performance of (MECs) in hydrogen production strongly depends on the applied voltage. An optimal range of 0.25-1.4V is required, as input voltages below or above this range may cause reduced hydrogen production and damage to the electrode material. Inhibiting the growth of methanogens with chemicals or antibiotics can increase biohydrogen production. Direct use of sewage sludge as a source of microbial population can also increase hydrogen formation. For example, studies have shown that the use of a monoculture of *Clostridium butyricum* in a MEC at a voltage of 0.6 V resulted in the formation of 3.2 mmol of hydrogen per hour at the anode. At the same time, the use of an association of *Clostridium acetobutylicum* and *Geobacter sulfurreducens* at the same voltage resulted in the formation of 4.8 mmol of hydrogen per hour at the anode. An optimal combination of parameters such as microbial selection and voltage can improve hydrogen production in MEC.

Temperature affects microbial selection and activity in biohydrogen production, with an optimum temperature of 35°C for exoelectric metabolism and growth. High temperature increases the formation of hydrogen, and in the process, there is also a simultaneous removal of pollutants [2].

**III. Combined use of dark enzymatic processes and microbial fuel cell for hydrogen production.** sDFMFC may be a more energy-efficient process for hydrogen production compared to water electrolysis, since water electrolysis requires 1.23–2.0 and sDFMFC requires less than 1 V. In addition, sDFMFC has an advantage in the output potential of hydrogen and can achieve an energy yield of as in methanogenesis. Also, in the sDFMFC process, biomass is converted to hydrogen and other biomolecules by DF, and CC is then oxidized by exoelectrics in the microbial film on the anode, which generates electricity, while ensuring efficient use of resources and recycling of waste.

The simultaneous process of DF and MFC in one reactor (sDFMFC), which is a hybrid process of DF and MFC, may be a promising strategy for industrial hydrogen production technology. In sDFMFC, feed substrates are converted to $H_2$, CC and other biomolecules by DF, and CC are then oxidized by exoelectrics in the microbial film on the anode, generating electricity. Degradation of complex substrates into smaller molecules, such as CC at the DF stage, would favor MFC reactions. In addition, the removal of CC by MFC can prevent the decrease in pH and the inhibition of CC. Therefore, an increased $H_2$ yield and energy conversion can be expected in the sDFMFC process. A significant improvement in $H_2$ production in a simultaneous DF and MEC process has previously been reported. A higher energy recovery of 17.3% was obtained from *S. japonica* with an $H_2$ yield of 110 of approximately 110 mL/g of volatile suspended solids (VS) at a maximum power density of 1.82 $W/m^2$, comparatively to the $H_2$ yield ($YH_2$) reached a maximum of 89.04 ± 2.1 mL/g-VS at 4th day of the non-combined DF operation.

**Conclusions.** Various approaches to increase the yield of hydrogen in biogenerators are considered. In particular, it is indicated that the optimal conditions for obtaining the maximum yield of hydrogen are 70°C and 0.25-1.4V in microbial electrolytic cells.

The monoculture of *Clostridium butyricum* made it possible to obtain 3.2 mmol of hydrogen per hour, and the association of *Clostridium acetobutylicum* and *Geobacter sulfurreducens* - 4.8 mmol of hydrogen per hour. Using sDFMFC for hydrogen production can be more energy efficient as it requires less voltage compared to water electrolysis.

Under the optimal conditions of using SVM-GA and SVM-PSO models - pH 6.75, the concentration of organic compounds that decompose glucose (GDOC) 16.16 g / l and temperature 37.55°C - it was possible to achieve a maximum hydrogen yield of 8.28 mol $H_2$ per kg of dry organic matter, which is 2.1 times higher than the output with non-optimized parameters. The combination of the fermentation process and the microbial fuel cell can be a promising method for reducing energy costs for hydrogen production and reducing its cost. Production parameters require further investigation to understand their impact on microbial activity and biogenerator production.

**References:**

1. Sarangi P. K., Nanda S. Biohydrogen Production Through Dark Fermentation. Chemical Engineering & Technology. 2020. Vol. 43, No. 4. P. 601–612.

2. Mahata C., Ray S., Das D. Optimization of dark fermentative hydrogen production from organic wastes using acidogenic mixed consortia. Energy Conversion and Management. 2020. Vol. 219. P. 113047.

3. Microbial electrolysis cells and microbial fuel cells for biohydrogen production: current advances and emerging challenges / A. Saravanan et al. Biomass Conversion and Biorefinery. 2020.

4. Co-production of hydrogen and electricity from macroalgae by simultaneous dark fermentation and microbial fuel cell / T. R. Gebreslassie et al. Bioresource Technology. 2021. Vol. 336. P. 125269.