

## ANALYSIS OF SYNTHETIC RENEWABLE METHANE PRODUCTION TECHNOLOGIES FOR IMPLEMENTATION IN UKRAINE

Klimenko V.N., Suprun T.T.

Institute of Engineering Thermophysics, National Academy of Sciences of Ukraine, Kyiv, [suprun@secbiomass.com](mailto:suprun@secbiomass.com)

*Methanation technologies for the production of synthetic renewable methane are considered. The possibilities of applying the methods of catalytic and biological methanation are analyzed. The implementation of methanation technologies is carried out with the efficient use of renewable energy sources. The Power to Gas concept for the generation of synthetic renewable methane in different countries are considered. Some results of studies of methanation processes, obtained in ongoing projects, are presented. World experience in the implementation of methanation technologies for the production of synthetic renewable methane can be an example for Ukraine.*

**Keywords:** synthetic renewable methane, methanation processes, the concept of Power to Gas, renewable energy sources

### Introduction

There is a growing interest in renewable energy sources in the modern world energy industry. These are solar energy, wind energy and biomass energy, which are an alternative to traditional energy sources - coal, natural gas and oil. However, a number of factors hinder the practical use of these sources. For solar and wind power plants that operate unstably in time (day-night, summer-winter, the influence of weather conditions), there are difficulties in coordinating their operating modes with electric networks. For biogas plants, direct transfer of the resulting biogas to existing gas networks is not possible due to the high (up to 50%) carbon dioxide content in biogas. Therefore, it is necessary to transform these types of renewable energy into a form that is compatible with the possibilities of their use. For solar and wind power plants, this is the accumulation of excess generated unstable electricity by generating synthetic methane - the so-called Power-to-Gas (PtG) process [1, 2].

The PtG technological chain is a three-stage energy conversion process. The first stage is to convert the primary energy from the sun, wind or biomass into electricity or biogas. The second stage uses renewable electricity and biogas to produce carbon dioxide and hydrogen. The methanation process, which converts CO<sub>2</sub> and H<sub>2</sub> into synthetic renewable methane, is the third final stage. Thus, synthetic renewable methane is an accumulator of used renewable energy.

*The purpose* of the publication is to analyze the experience of foreign countries in obtaining synthetic renewable methane and to determine the most effective technologies for implementation in Ukraine.

*Research methods* include the study and analysis of literature and other data, in particular, methanation projects. Ukraine has great potential and prospects for the development of biomethane production [3], so the use of world experience in the implementation of the PtG concept is an important issue for our country.

### 1 Methanation process

There are two methods of methanation technology as the basis of PtG processes:

- in catalytic reactors in which the Sabatier chemical reaction is implemented;
- in biological reactors, where the methanation process occurs with the participation of methanogenic microorganisms, the so-called archaea.

Studies of methanation processes in both of these directions are carried out in many countries: the USA, Switzerland, Denmark, Germany, France, Japan, and others. Laboratory, pilot and demonstration installations that implement the ideas of PtG are already known.

### 1.1 Catalytic methanation

Catalytic methanation – is a chemical reaction in which hydrogen and carbon dioxide are synthesized into methane. The production of methane through the Sabatier reaction (1) is an exothermic catalytic reaction and usually takes place at temperatures from 200°C to 550°C:



To improve the efficiency of methanation, numerous studies have been carried out to develop catalysts with high activity, CH<sub>4</sub> selectivity and stability under conditions of heat release during the reaction. Such catalysts as Nickel, Ruthenium, Rhodium, Palladium, Cobalt, Iron were considered [4].

Reaction (1) is highly exothermic, so the adiabatic temperature rise associated with the reaction is quite high. This increase in temperature leads to a decrease in the proportion of H<sub>2</sub> and CO<sub>2</sub> that have reacted (i.e., to a decrease in the amount of methane generated or the rate of methanation). To increase the yield of methane, it is necessary to lower the temperature of the methanation process, as well as to increase the pressure in the reactor. The search for economically feasible ways to lower the operating temperatures of the methanation process is one of the main issues in creating an acceptable technology for the PtG process.

For catalytic methanation various types of reactors are used. In cooled fixed-bed reactors [1] the working process takes place in cylindrical tubes with a catalyst, which are washed on the outer surface with a coolant of a given temperature. In this case, water can be used as a coolant, but its main drawback is the dependence of the boiling point on pressure, i.e. high temperatures require high pressure. Other concepts are based on the use of three-phase reactors for methanation [5]. In suspension reactors, the working zone is filled with heat-transfer liquids, in which small particles of the catalyst go into a state of suspension due to the gas flow. The high heat capacity fluid allows almost complete removal of the heat of the reaction, ensuring practically isothermal operation of the methanator.

A disadvantage of fixed bed adiabatic reactors is the appearance of high temperature and high pressure drop zones. To overcome these shortcomings, structured reactors such as monolithic reactors have been developed [6]. The use of an internal metal structure made it possible to increase heat transfer in the working area by two to three orders of magnitude.

Microchannel reactors [7] are a modification of structured reactors. The advantages of such reactors are compactness and good thermal control. Compactness is ensured by an increased ratio of the surface of the metal microstructure to its volume. Ru-TiO<sub>2</sub> in powder form was used as a catalyst. The application of a catalyst to a metal structure, as well as the removal of the used catalyst, make it difficult to operate such reactors.

### 1.2 Biological methanation

The process of biological methanation is carried out using archaea of the genus *Methanothermobacter* as catalysts capable of converting hydrogen and carbon dioxide into synthetic methane. Biological methanation takes place in anaerobic conditions at atmospheric pressure and temperatures from 20 to 65°C. There are two concepts of the biological methanation process:

– *In situ* methanation, i.e. in a biogas reactor, where hydrogen is directly supplied from some external source:

– *Ex-situ* methanation in a special reactor - a methanator, where biogas (a mixture of 50-60% methane and 40-50% carbon dioxide), hydrogenotrophic methanogens, and hydrogen are supplied separately. Alternative CO<sub>2</sub> can also be supplied here.

During *in-situ* methanation, hydrogen from an external source (electrolyzer) is fed into the lower part (bottom) of the reactor, blown through the fermentation liquid, where with the help of archaea, it methanizes CO<sub>2</sub>, which is released in the process of anaerobic fermentation of biomass. Intensive stirring of the fermentation liquid activates the process. As the conducted studies have shown, it is extremely difficult to achieve complete conversion of CO<sub>2</sub> released during the fermentation process.

Within the framework of the BTU-FESPE project of the Brandenburg University of Technology, the process of biocatalytic methanation in an anaerobic trickled-bed reactor was investigated [8]. Such a reactor contains a packed bed as a surface on which microorganisms can be immobilized. A three-phase system is formed on the carrier surface (biofilm–liquid–gas). Thus, in the anaerobic trickle-bed process, methane with a concentration above 98% can be obtained [8].

An article by research organizations in Ireland [9] published the results of studies on *in-situ* and *ex-situ* biological methanation to produce synthetic renewable methane that can be fed into existing gas networks. The work [9] proposes a sequential combination of several *ex-situ* blocks, as well as a hybrid model for combining *in-situ* and *ex-situ* blocks, taking into account the advantages and disadvantages of each of these concepts. The paper [10] also considers various systems and technologies for biological methanation, such as *in-situ* and *ex-situ*. The main parameters that determine the cost-effectiveness of each technology, as well as ways to optimize them, are noted.

### 1.3 Comparison of biological and catalytic methanation

Comparison of biological and catalytic methanation technologies was carried out in many works. In particular, in a review [2] these comparisons were made according to the following indicators:

- The volume of the reactor required to ensure the same productivity;
- Resistance to the influence of impurities;
- Dependence of the methanation process on the load;
- Energy efficiency.

The results of these studies showed that:

- The volume of the catalytic methanation reactor is less than the volume of the biological methanation reactor required to provide the same productivity;
- Biological methanation is more resistant to impurities. Contaminants such as sulfur and oxygen do not affect biological methanation, while in catalytic methanators sulfur and its compounds are harmful to nickel catalysts;
- Fixed-bed reactors are the most sensitive to load changes due to catalyst temperature fluctuations. The liquid phase present in biological and three-phase methanation buffers the effect of load changes;
- Considering that catalytic methanation does not require a stirrer and can use waste heat, this technology is more efficient.

## 2 Implementation of the PtG concept in pilot, demonstration and laboratory plants

In [11], a detailed review of PtG projects implemented in different countries is made. The largest number of projects during 2009-2019 was carried out in Germany and concerned both catalytic and biological methanation. Among other countries, the leadership is held by Great Britain, Denmark, Switzerland, the USA, Austria, Japan and others.

### 2.1 PtG projects with catalytic methanation

One of the largest PtG plants in Germany with a capacity of 5 MW Audi e-gas uses catalytic methanation technology in one isothermal fixed-bed reactor [12]. Renewable electricity for electrolysis comes from four wind turbines and CO<sub>2</sub> is generated in upgrading process at nearby biogas plant. The efficiency of the PtG process is 54% without taking into account additional thermal energy produced. The wind power plant itself, unlike a biogas plant, is not used permanently, but according to the power supply scheme. The plant is now qualified for participating in what is known as the electricity balancing market [13].

The idea of increasing the efficiency of PtG technology by thermally integration of high-temperature electrolysis with catalytic methanation at high pressure was implemented in the project HELMETH [14] (Fig.1). The project brings together partners from Germany, Italy, Greece and Belgium.

The efficiency of the PtG process was expected to be increased from 61% (using conventional electrolyzers and low-pressure catalytic methanation) to 85% and higher at pressures up to 30 bar and a high-temperature electrolyzer on the base of SOECs. The heat of the exothermic methanation reaction was used in the process of high-temperature electrolysis under pressure, which increased the efficiency of the PtG process. To achieve a high methane yield, the HELMETH project tested and optimized various nickel and ruthenium catalysts, which ensured the content CH<sub>4</sub> in the methanation product at a level of more than 97 vol.-%, and hydrogen concentrations below 2 vol.-%.

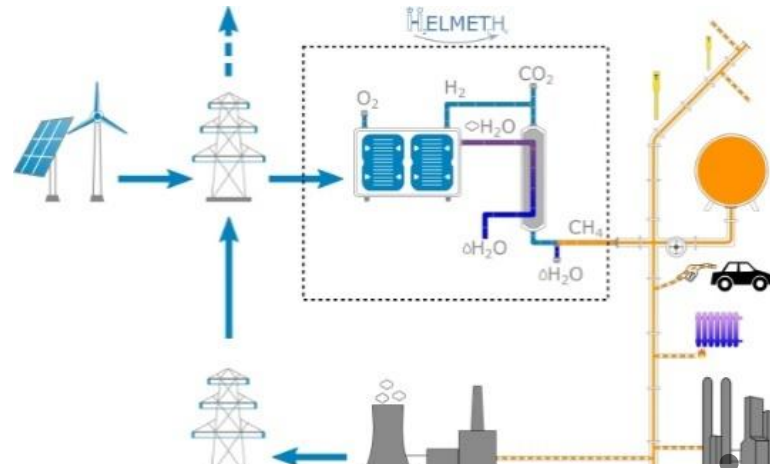


Fig.1. HELMETH PtG concept [14]

## 2.2 PtG projects with biological methanation

The first biomethanation-based PtG concept to reach commercial status in the world is the Bio Power 2 Gas project. It was started in 2013 and implemented in 2015 in Allendorf (Germany). Viessmann group subsidiaries provided equipment for this plant [15]. Before the implementation of the project, laboratory studies were carried out that confirmed the viability of the concept of biological methanation (the methane content in biogas increased from 60 to 95%). Thus, biological methanation of pure CO<sub>2</sub> and H<sub>2</sub> was realized in this project.

A significant recent event (April 28-29, 2022) was the official inauguration of Europe's first industrial PtG plant in Switzerland. Based on biological methanation, this plant is the first in Europe and is an important milestone both for its owner and operator Limeco and for HZI Schmack (a subsidiary of Hitachi Zosen Inova AG), which proposed the innovative technology [16]. The new PtG plant uses renewable electricity from a wastewater treatment plant to split water into oxygen and hydrogen using electrolysis. In the second stage of the process, this hydrogen is fed to the HZI Schmack methanation reactor together with the waste water gas. In the "BiON" process the microorganisms in this bioreactor convert hydrogen and CO<sub>2</sub> contained in wastewater gases into biomethane under anaerobic conditions. The biomethane is then purified and can be fed into the local gas network as a CO<sub>2</sub>-neutral substitute for natural gas.

## Conclusion

In modern conditions, the production of synthetic renewable methane, which are an alternative to expensive and sometimes scarce natural gas, is of great importance. The current PtG system can be considered as a main generator of synthetic renewable methane. Today, in many countries of the world (Germany, Great Britain, Denmark, Switzerland, USA, Austria, Japan, the Netherlands and others), active work is underway to create technologies that implement the concept of PtG. Numerous laboratory, pilot and demonstration projects have already been carried out, confirming the viability and promise of the PtG concept.

The main efforts of researchers are aimed at increasing the efficiency of hydrogen generation and methanation processes, as well as increasing the productivity of electrolyzers and methanators. For example, for adiabatic catalytic methanation reactors, the main problem is ensuring the optimal reaction temperature due to cooling. However, for instance, a three-phase reactor is devoid of this disadvantage. For biological methanation reactors, the main problem remains the low level of mass transfer of hydrogen, which limits the productivity of the process.

The PtG concept involves the production of synthetic renewable methane by catalytic or biological methanation, i.e., combining hydrogen with carbon dioxide using surplus energy from renewable energy sources to generate hydrogen in certain electrolyzers.

Comparing the results of the implemented PtG projects with catalytic and biological methanation processes, we can draw the following conclusions:

– Medium to large PtG projects (over 1MW) are being implemented using catalytic methanation technology due to their scalability and the ability to increase process efficiency by using the heat of methanation.

– Small-capacity projects should be implemented using biological methanation, because biomethanation requires the use of reactors with a large specific volume. However, its increased resistance to such harmful impurities as sulfur and oxygen compensates this direction of biomethanation.

– Both biomethanation concepts of PtG – *in-situ* and *ex-situ* – have found their practical implementation. The hybrid model *in-situ* + *ex-situ* takes advantage of each of these concepts.

The world experience of implementing the PtG concept should become an example for Ukraine. A separate task of this study was to determine the most appropriate methanation technologies for the production of synthetic renewable methane in Ukraine. It should be noted that in recent years there has been an increased interest in biogas technologies in Ukraine. To date, more than 70 biogas plants have already been built in the country. Therefore, it is quite logical and economically justified to use biomethane technologies for the production of synthetic renewable methane. For example, such a plant may combine a biogas reactor as a source of carbon dioxide, which is an integral part of the resulting biogas, with an *ex-situ* methanation process, where either biological or catalytic methanation is used. This way of developing bioenergy can be a powerful incentive for the construction of solar and wind power plants as sources of electricity for producing renewable hydrogen used in the methanation process. However, to get a final answer to the question - which of the technologies can be recommended for implementation in Ukraine, is possible only based on a feasibility study of synthetic renewable methane production technologies.

## REFERENCES

- 1 Schaaf T., Grünig J., Schuster M.R., et al. Methanation of CO<sub>2</sub> - storage of renewable energy in a gas distribution system. *Energ Sustain Soc.*, 2014, 4. doi: 10.1186/s13705-014-0029-1
- 2 Gotz M., Lefebvre J., Mors F., et al. Renewable power-to-gas: A technological and economic review. *Renewable Energy*, 2016. 85, pp. 1371-1390. doi:10.1016/j.renene.2015.07.066
- 3 Geletukha G., Kucheruk P., Matveev Yu. Prospects and potential for biomethane production in Ukraine. *Ecological Engineering & Environmental Technology*. ISSN 2719-7050. 2022, Vol. 23, Is. 4, pp. 67–80. <http://www.ecoet.com/Prospects-and-Potential-for-Biomethane-Production-in-Ukraine,149995,0,2.html>
- 4 Tan C.H., Nomanbhay S., Shamsuddin A.H., et al. Current Developments in Catalytic Methanation of Carbon Dioxide – A Review. *Front. Energy Res.*, 2022. Vol. 9:795423. doi:10.3389/fenrg.2021.795423
- 5 Lefebvre J., Gotz M., Bajohr S., et al. Improvement of three-phase methanation reactor performance for steady-state and transient operation. *Fuel Process. Technol.*, 2015, 132, pp. 83 – 90. doi:10.1016/j.fuproc.2014.10.040
- 6 Janke C., Duyar M.S., Hoskins M., et al. Catalytic and adsorption studies for the hydrogenation of CO<sub>2</sub> to methane. *Appl. Catal. B Environ.*, 2014. 152-153, pp. 184-191. doi:10.1016/j.apcatb.2014.01.016
- 7 Brooks K.P., Hu J., Zhu H., et al. Methanation of carbon dioxide by hydrogen reduction using the Sabatier process in microchannel reactors. *Chem. Eng. Sci.*, 2007. 62, pp. 1161-1170. doi:10.1016/j.ces.2006.11.020
- 8 Burkhardt M., Koschack T., Busch G. Biocatalytic methanation of hydrogen and carbon dioxide in an anaerobic three-phase system. *Bioresour. Technol.*, 2014. 178, pp. 330-333. doi: 10.1016/j.biortech.2014.08.023
- 9 Voelklein M.A., Rusmanis D., Murphy J.D. Biological methanation: Strategies for in-situ and ex-situ upgrading in anaerobic digestion. *Applied Energy*, 2019, 235, pp.1061-1071. doi: 10.1016/j.apenergy.2018.11.006
- 10 Rusmanis D., O'Shea R., Wall D.M., et al. Biological hydrogen methanation systems – an overview of design and efficiency. *Bioengineered*, 2019, 10:1, pp. 604-634. doi: 10.1080/21655979.2019.1684607
- 11 Bailera M., Lisbona P., Romeo L.M., et al. Power-to-gas projects review: Lab, pilot and demo plants for storing renewable energy and CO<sub>2</sub>. *Renewable and Sustainable Energy Reviews*, 2017, Vol. 69, pp. 292-312. doi.org/10.1016/j.rser.2016.11.13
- 12 Rieke S. Catalytic methanation – the Audi e-gas project as an example of industrialized technology for Power to gas. *REGATEC*, 2015, Barcelona, Spain, 2015.
- 13 Strohbach O. Audi e-gas plant stabilizes electrical grid. *Press Release - Audi MediaInfo - Technology and Innovation Communications*; 2015. <https://www.automobilsport.com/audi-e-gas-stabilizes-electrical-grid---138930.html>
- 14 Project HELMETH. <http://www.helmeth.eu/index.php/project>
- 15 Heller T. Thomas Heller, Power-to-Methane Joint Workshop - Renewable Energy House, Brussels, 06.09.2017. <https://www.gie.eu/wp-content/uploads/filr/3234/4.%20Thomas%20Heller-Microb%20Energy.pdf>
- 16 <https://bioenergyinternational.com/europes-first-industrial-biological-methanation-ptg-plant-inaugurated>