HYDROGEN SUPPORTED BIOCONVERSION OF BIOGAS CO_2 TO UPGRADE BIOMETHANE IN FUEL FOR VEHICLES: RECENT FINDINGS IN FARMERS SURVEY

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Abstract. Biogas is a fuel obtained from organic waste fermentation in an anaerobic digestion plant and can be burned in a cogeneration unit to produce heat and electricity. In Latvia, biogas plants are popular among farmers, as electricity is mostly sold to the centralized electricity grid, receiving a subsidy in the form of a mandatory procurement component. Political circles are discussing the reduction or even abolition of this support, so the question of where to put the produced biogas is topical. Recently, many European countries have incentivized the production of biomethane to be injected into natural gas grids or compressed and used as biofuel in vehicles. The implementation of biogas upgrading unit into an existing anaerobic digestion plant to convert biogas to biomethane (<97%) can be performed by means of various technologies, physical and chemical absorption, adsorption, membrane and cryogenic separation. There are also biological pathways for biogas upgrading - biological conversion of residual CO_2 and external hydrogen to methane carried out by hydrogenotrophic methanogens. The aim of this research is to give a review about latest developments in technologies and update views of biogas producers on possible upgrading of bio-methane concentration in the fermentation process. The main research results have indicated that farmers have interest in technological achievements of biological CO_2 reformation, as well as specific changes in the fermentation process. They are supporting production of new kind of renewable fuel with possible application for vehicles, also indicate high costs in reformation and mechanical separation processes.

Keywords: biogas, biomethane, bio-upgrading, hydrogen, survey.

Introduction

Latvia's National Energy and Climate Plan is a national roadmap for both business and society: it marks the direction we will take by 2030 [1] and is tightly connected with the Paris Agreement of 2015, where crucial pillar is the reduction of greenhouse gas (GHG) emissions [2]. This target was transferred to national targets and strategies for GHG emission reduction - the European Union (EU) and its member countries set increasingly ambitious GHG-emission reduction targets for 2020, 2030, and 2050. This strategy has been reinforced by the European Commission Green Deal roadmap [3], setting more ambitious environmental targets. One pathway to reach GHG-emission reductions is the increase and further deployment of renewable energy systems (RES). Technologies of them contribute to emission reduction compared to fossil energy systems [4]. Energy from biomass has the largest share of RES carriers in the world [5]. Bioenergy is provided via solid, liquid, and gaseous energy carriers. Although biogas plays a minor role (2%) compared to solid bioenergy carriers (89%), global biogas production is increasing rapidly. About half of the global biogas production capacity is located in Europe [6]. Biomethane could be named as one of the most promising for short and mid-term transport decarbonisation solutions both in the EU and Latvia [7].

In this article the review about latest developments in biological hydrogen methanation (BHM) approaches where external H2 is coupled with CO2 from the biogas production process to form CH4 is given. Unlike commercially available physical CO2 separation methods from biogas, which are being implemented in many biogas plants around the world, BHM technology, although still in the research phase, makes it possible to reduce or even eliminate CO2 emissions. A survey is performed to find out if farmers have interest in technological achievements of BHM in biological CO2 reformation, as well as specific changes of purpose of biogas use.

Biogas upgrading – traditional methods

Upgrading of biogas to biomethane traditionally is done by removing components like water, hydrogen sulphide, ammonia, oxygen, nitrogen, carbon monoxide, halogenated hydrocarbons, siloxanes, and particles in the first stage. In the second stage, carbon dioxide (CO_2) is removed for the increment of the methane (CH_4) content [6]. Currently, biogas upgrading is starting with water scrubbing, chemical scrubbing, and physical scrubbing at the first stage, after what the biogas is ready for combustion to produce electricity and heat in cogeneration. Water scrubbing represents the highest

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share in Europe, with about 40% [6]. The scrubber utilises a mixture of caustic soda, polyvinyl alcohol and water as desulfurization solvent. Then, an activated carbon filter allows removing the remaining traces of H_2S and VOCs (Volatile Organic Compounds). At the second stage biogas is upgraded to biomethane using pressure swing adsorption (PSA) or membrane separation technologies. Zeolites adsorb strongly carbon dioxide and weaker - methane, therefore it can be applied as an effective CO_2 adsorbent in PSA applications [8]. Another promising approach is currently seen in cryogenic upgrading technologies, in which simultaneously can be obtained high-purity biomethane and food-grade CO_2 [9]. All mentioned techniques for biogas upgrading are available on the market at different development stages - four of them are well-known: water scrubbing, membrane separation, chemical absorption and pressure swing adsorption, but others are less widespread - organic physical scrubbing, cryogenic separation technologies, hot potassium carbonate and biological methods [10]. All these technologies can be characterised as energy-intensive processes, having an energy demand ranging from 0.05 $kWhe \cdot (Nm^3)^{-1}$ to 0.76 $kWhe \cdot (Nm^3)^{-1}$ raw biogas [11].

Biogas upgrading – biochemical methods

Recent advantages have been made in the field of biochemical biogas upgrading [12-15]. Those encompass biological hydrogen methanation (BHM) approaches where external H_2 is coupled with CO_2 from the biogas production process to form CH_4. According to the Sabatier reaction (Eq. (1)), hydrogenotrophic methanogenic archaea is able to consume an equimolar amount of four times hydrogen (H_2) to carbon dioxide (CO_2) and generate biomethane of natural gas quality [12].

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O,\ \Delta G^0 = -165\ kJ \cdot mol^{-1} \tag{1}$$

For this purpose, H_2 can be produced by water electrolysis using the surplus of electricity generated from windmills or photovoltaic facilities [13]. The circular economy combination of hydrogen produced via electrolysis of curtailed/constrained electricity, biogas production from the digestion of organic waste upgraded to gas grid specification through the reaction of biogas and the aforementioned hydrogen provides a decentralized form of energy storage [13].

This can be done either by direct injection of H_2 into the anaerobic digester or by injection of H_2 into a separate bioreactor. Both approaches can also be combined. The biological hydrogen methanation (BHM) process utilizes this reaction, catalysed by specific archaea of methanothermobacter genus, capable of converting H_2 and CO_2 to CH_4 with water as a by-product. This biological method of CO_2 conversion could potentially eliminate the traditional energy-intensive CO_2 separation processes in AD, whilst allowing for the potential doubling of the CH_4 yield (depending on biogas composition) [13].

The BHM process is capable of being carried out both within an anaerobic digester system known as in-situ, or in a separate, adjacent reactor known as ex-situ [12-15]. In-situ bio-methanation takes place within the anaerobic digester. H_2 gas is introduced typically through mixing or diffusion to maximize the contact area with hydrogenotrophic methanogenic archaea, which produce CH_4 from CO_2 and H_2. Standard anaerobic digestion of feedstock also occurs within the reactor, providing nutrients, contained within the digested substrates, and also CO_2, needed by various microbes through acetogenesis, methanogenesis and methanation.

Ex-situ methanation takes place in a separate external reactor, typically tailored to suit the hydrogenotrophic methanogens and can be used also in case of biomass gasification [15]. Specific nutrient media are supplied to the microbial consortium, under a controlled environment. Gaseous reagent supply is also maintained to ensure optimal growth conditions and product concentrations. Gas purification remains to ensure grid quality gases and includes remove of water vapour.

To allow H_2 uptake by archaea, the BHM can be characterised as energy-intensive technology due to the processes which are required for effective H_2 solubilisation, such as intense mixing from impellers, compressors and recirculation of gas and liquids. This results in higher parasitic energy demands for the upgrading process. The scientific literature suggests the agitation as a method of hydrogen solubilisation in the liquid for BHM [12-14]. However, agitation constitutes a large energy demand for these BHM systems. This is further compounded by the requirement for continuous operation, i.e. minimum power consumption of the plant can be assumed to be the power demand of the mixing component at an idle stage. At a large scale, the use of high rate agitation to promote H_2 solubilisation may be justified [13].

Number of demonstration projects are realised in 2013-2018 (Denmark, Germany) and experience summary available (see, for example, [16-17]).

Materials and methods

Research methods applied: analysis of scientific research findings reflected in scientific publications, policy documents and scientific research reports and analysis of expert survey results. For statistical analysis of expert survey methods of descriptive statistical analysis are applied: indicators of central tendency or location and indicators of variability, as well as cross tabulations.

Survey results and discussion of biogas producers in Latvia

Latvia has high biogas installed electric capacity per 1 million of population, generated in 48 biogas stations (data on 01.06.2020). Most of them were built during 2009-2015, when also 5 biogas plants during this period were shut down [18]. The biogas is mostly used for production of electricity, however, transformation of biogas into biomethane for use in transport would be regarded as a more cost-effective option in terms of economy than combustion of biogas locally [7].

Questionnaire for the survey has been developed taking into account research findings reflected in the scientific publications and according to the legislative regulations and interests by the representative public administration to prepare better reasons for decision making. A pilot survey was conducted, and questionnaire was improved to prepare more precise statements understandable for all respondents. The survey was conducted during the period January –March, 2021. From all biogas producers in Latvia for 35 the production permissions were found in the database of the State Environmental Monitoring Bureau, and they were approached, for several producers there were three invitations (after one week and then once more after two weeks) to answer the questions. During the survey 10 responses on the survey questions were received. The main statistical indicators on responses on the question “For what practical reason was created your biogas production?” are included in Table 1.

Table 1

Main statistical indicators on responses to question “For what practical reason was created your biogas production?”

Statistical indicators		(1)*	(2)	(3)	(4)	(5)	(6)	(7)	(8)
N	Valid	8	8	8	10	8	9	9	8
	Missing	2	3	3	0	2	1	1	2
Mean		1.00	2.13	4.88	8.90	1.75	2.89	6.22	3.38
Std. Error of Mean		0.000	1.125	1.575	0.900	0.750	1.047	1.412	1.451
Median		1	1	3	10	1	1	8	1
Mode		1	1	1	10	1	1	10	1
Std. Deviation		0.000	3.182	4.454	2.846	2.121	3.140	4.236	4.104
Range		0	9	9	9	6	9	9	9
Minimum		1	1	1	1	1	1	1	1
Maximum		1	10	10	10	7	10	10	10

* (1) – For car refuelling
(2) – For production of heat/cold
(3) – For electricity generation
(4) – For electricity/heat cogeneration
(5) – For input into the natural gas network
(6) – For own consumption
(7) – For own consumption and sale
(8) – For sale

Source: Authors calculations based on survey in 2021, evaluation scale 1-10, where 1- full disagreement; 10 – full agreement.

The data of Table 1 indicate that most of respondents have created their production of biogas for electricity and heat cogeneration; for own consumption and sale, several producers have created it for electricity generation, but nobody from respondents has created their production for biogas for car refuelling. The main statistical indicators on responses to the question “Do you think about the change of aims of biofuel production in today’s situation (reduction of OIK, etc)?” are included in Table 2.

Table 2

Main statistical indicators on responses to question "Do you think about the change of aims of biofuel production in today's situation (reduction of OIK, etc)?"

Statistical indicators		(1)*	(2)	(3)	(4)	(5)	(6)
N	Valid	9	8	9	8	9	9
	Missing	1	2	1	2	1	1
Mean		7.00	3.88	2.78	3.75	6.56	4.11
Std. Error of Mean		0.882	1.156	0.862	0.940	0.835	1.274
Median		7	3	1	4	7	1
Mode		7	1	1	1	7	1
Standard Deviation		2,646	3.271	2.587	2.659	2.506	3.822
Range		9	9	7	7	9	9
Minimum		1	1	1	1	1	1
Maximum		10	10	8	8	10	10

* (1) – For car refuelling
(2) – For production of heat/cold
(3) – For production of bio-hydrogen
(4) – For electricity generation
(5) – For electricity/ heat cogeneration
(6) – For input into the natural gas network

Source: Authors calculations based on survey in 2021, evaluation scale 1-10, where 1- full disagreement; 10 – full agreement

The data of Table 2 indicate that most of respondents are planning to contribute with their produced biogas for care refuelling and for electricity and heat cogeneration, but only few are planning production of biogas for input into natural gas network and also only few producers plan to change their aims on production of biogas and planning for production of bio-hydrogen. The main statistical indicators on responses to question "Do you plan investment into modernisation of technologies in production?" are included in Table 3.

Table 3

Main statistical indicators on responses to question "Do you plan investment into modernisation of technologies in production?"

Statistical indicators		(1)*	(2)	(3)	(4)	(5)	(6)	(7)	(8)
N	Valid	9	8	8	8	8	9	8	8
	Missing	1	2	2	2	2	1	2	2
Mean		4.11	3.00	2.63	3.88	1.50	6.78	2.00	1.63
Std. Error of Mean		1,306	0.845	0.905	0.854	0.267	0.846	0.627	0.324
Median		1	2	1.5	4.5	1	8	1	1
Mode		1	2	1	5	1	8	1	1
Standard Deviation		3.919	2.390	2.560	2.416	0.756	2.539	1.773	0.916
Range		9	7	7	7	2	8	5	2
Minimum		1	1	1	1	1	1	1	1
Maximum		10	8	8	8	3	9	6	3

* (1) – Introduction of bio-methane into the natural gas network
(2) – Larger storage of bio-methane (underground or elsewhere)
(3) – Production of bio-hydrogen
(4) – Biological upgrading of bio-methane
(5) – Cogeneration in molten salt or solid oxide fuel cells (MCFC and SOFC)
(6) – Compressed bio-methane for car refuelling
(7) – Charge electric cars
(8) – Refuelling electric/hydrogen cars

Source: Authors calculations based on survey in 2021, evaluation scale 1-10, where 1- full disagreement; 10 – full agreement

The data of Table 3 indicate that most of respondents are planning to invest in technologies to produce compressed bio-methane for car refuelling and some of biogas producers are planning to invest in technologies for biological upgrading of bio-methane, but very little interest is to invest in technologies for cogeneration in molten salt or solid oxide fuel cells (MCFC and SOFC respectively). The main statistical indicators on responses to question “Are you interested in modernizing technology?” are included in Table 4.

Table 4

Main statistical indicators on responses “Are you interested in modernizing technology?”

Statistical indicators		I think about technology upgrades	I follow the research results in scientific journals abroad	I follow the research results in Latvian science	I collaborate with scientists
N	Valid	10	9	9	9
	Missing	0	1	1	1
Mean		8.50	5.44	5.00	4.00
Standard Error of Mean		0.401	0.689	0.601	1.080
Median		8.5	5	5	2
Mode		7 and 10	5	5	2
Standard Deviation		1.269	2.068	1.803	3.240
Range		3	7	6	9
Minimum		7	2	2	1
Maximum		10	9	8	10

Source: Authors calculations based on survey in 2021, evaluation scale 1-10, where 1- full disagreement; 10 – full agreement

The data of Table 4 indicate that most of respondents are planning to think about technology upgrades, many of them follow the research results in scientific journals abroad, several respondents follow the research results in Latvian science, but not so many biogas producers collaborate with scientists – here is the biggest variability of respondents’ evaluations – all evaluation scale covered with arithmetic mean of evaluations was 4, mode was 2 (most often given evaluation) and median was 2 (half of respondents evaluated by 2 or less and half of respondents have evaluated by 2 and more).

Table 5

Distribution of responses on “I think on technology upgrades” and years in bio-gas production

Evaluations	Years in bio-gas production					Total
	6	7	8	10	13	
7	0	0	0	2	0	2
8	1	0	0	1	0	2
9	0	0	0	1	1	2
10- definitely yes	0	1	1	1	0	3
Total	1	1	1	5	1	9

Source: Authors’ calculations based on survey in 2021, evaluation scale 1-10, where 1- full disagreement; 10 – full agreement

The data of Table 5 indicate that producers think about technology upgrades not depending from the years of operating in the production of biogas. Results of correlation analysis between evaluations on initial plans when the company was created and changes in plans for car refuelling (Table 6), which is very common with Sweden and Italy, where the main end-use application is transport [18].

Table 6

Correlation between evaluations on initial plans (created) and changes in aims (plans)

Indicators of correlation analysis		For own consumption and sale (created)	For car refuelling (plans)
For own consumption and sale (created)	Pearson Correlation	1	0.703*
	Sig. (2-tailed)		0.035
	N	9	9
For car refuelling (plans)	Pearson Correlation	0.703*	1
	Sig. (2-tailed)	0.035	
	N	9	9

Source: Authors' calculations based on survey in 2021, evaluation scale 1-10, where 1- full disagreement; 10 – full agreement

* Correlation is significant at the 0.05 level (2-tailed)

The data of Table 6 indicate that there is a statistically significant correlation between initial plans when the company was created and changes in future plans – production of bio-fuel for car refuelling.

Conclusions

Most of biogas producers have created (six to thirteen years ago) their production of biogas for electricity and heat cogeneration; for own consumption and sale, several producers have created it for electricity generation, but nobody has created their production of biogas for car refueling.

Recently (in 2021) the aims of producers are changed, and the most possible way is production of biogas for car refueling, which is very common with Sweden and Italy.

Most of biogas producers think about technology upgrades, they follow achievements in scientific findings, but not so many producers of biogas co-operate with scientists.

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