Periodica Polytechnica Chemical Engineering, 66(4), pp. 596–608, 2022

Efficiency Increase of Biological Methanation based Power-to-Methane Technology Using Waste Heat Recovery with Organic Rankine Cycle

Axel Groniewsky^{1*}, Réka Kustán¹, Attila Imre^{1,2}

² Department of Thermohydraulics, Centre for Energy Research, P. O. B. 49, H-1525 Budapest, Hungary

* Corresponding author, e-mail: groniewsky@energia.bme.hu

Received: 09 May 2022, Accepted: 11 August 2022, Published online: 30 August 2022

Abstract

Due to the efforts of reducing greenhouse gas emissions, nearly two-thirds of the installed electric capacity worldwide will come from renewables in 2050 (EIA 2021), making frequency control without energy storage impossible. Power-to-Methane (PtM) technology allows electricity to be stored in the form of methane. The storage efficiency of PtM may be increased either by maximizing the recovery of the stored electricity, which is a common method, or by reducing the amount of electricity the PtM has to be charged with for a given amount of stored energy. In this paper, a case study is presented for the latter by directly integrating an Organic Rankine Cycle into the PtM technology by recycling the waste heat from water electrolysis and biological methanation back to electrolysis. With this method, total storage efficiency can be increased by approximately two percentage points.

Keywords

Power-to-Methane, Organic Rankine Cycle (ORC), energy storage, efficiency improvement

1 Introduction

Based on the EIA 2021 report [1], 61.5% of the nearly 7200 GW of installed electric capacity in 2020 comes from conventional fossil fuels (oil, gas, coal), while renewables will account for one-third. Due to the efforts of reducing greenhouse gas emissions, this ratio is expected to level off by 2030 and reverse by 2050. The primary reason for the rebalancing may be that while consumption is expected to grow by more than 30% over the next ten years, fossil fuelbased electricity generation will stagnate in nominal terms, and renewable-based capacity will double till 2030 and almost quadruple by 2050. In the coming decades, renewables are expected to grow mainly from solar energy – from 21.3% to 52.8% of the total till 2050 – and a lesser extent from wind energy (from 24.8% to 26.9% till 2050).

The high penetration of renewable energy sources (RESs) into present power systems will affect the power system frequency. The type and design of the energy storage systems [2], the optimal location [3, 4], and sizing are essential to facilitate RES integration [5, 6] and solve various issues of power networks. In terms of the form of energy

stored, in this range, a distinction can be made between mechanical, electrochemical/electrical, and storage based on alternative low-carbon fuels, including Power-to-Liquid (PtL) and Power-to-Gas (PtG) technologies, depending on the phase (liquid or gas) of the energy carrier [7–9].

PtG is a generic term that encloses converting energy into hydrogen (PtH) or methane (PtM) (or rarely into other gases, like ammonia). The resulting compounds are mainly used as energy carriers, but further use is also possible as chemical feedstock [10]. As H_2 is an intermediate product of PtM, which in itself can be used for energy storage, doubts may arise about the usefulness of this technology (i.e., the need to convert H_2 any further). Namely, the longer the conversion chain, the greater the losses in the conversion process, yet the greater the value of the final product.

PtM technology has several advantages over PtH. PtM technology has the flexibility to handle fluctuating feed-in using the infrastructure of the already established natural gas networks, so unlike PtH technology, where energy-efficient, financially and technologically favorable H,

¹ Department of Energy Engineering, Faculty of Mechanical Engineering, Budapest University of Technology and Economics, Műegyetem rkp. 3, H-1111 Budapest, Hungary

storage and transport solutions are still to be found, PtM is suitable for long-term and large-scale energy storage with lower losses than in case of electrical energy [10, 11]. CH_4 has a higher energy density than H_2 which is an additional advantage for storage and transport. H_2 has a higher adiabatic flame temperature than CH_4 so direct combustion is only possible with dedicated burners, possibly with blending with other fuels.

The spread of PtM technology may be hindered by the low amount of pure CO_2 needed to produce biomethane and the lower conversion efficiency compared to PtH. Conversion efficiencies (energy input (HHV) vs. the energy input) vary between 64–77% for H₂ without compression (electrolysis) and between 51–65% for CH₄ conversion [12].

It should be noted that when the input electricity is carbon-free, H_2 (as a fuel or energy carrier) is also considered to be carbon-free. It seems to be a considerable advantage for PtH over PtM, because for PtM, CO_2 is always emitted during the energy recovery. However, this issue can be solved by choosing the proper CO_2 source for the methanation. Using CO_2 from renewable (therefore effectively carbon-free) origin, like biogas, the PtM method can also be considered net carbon-free because the input and output CO_2 (input during methanation, output during energy recovery) will be identical [13].

recovery) will be identical [13]. Total storage efficiency $(\eta = \frac{E_{out}}{E_{in}})$ is essential factor for all energy storage technologies. For PtG and PtF (Power-

to-Fuel) technologies, the traditional way to increase this number is to increase the amount of recovered energy (E_{out}) . For example, in PtM, it can be done by recovering the electricity from methane by high-efficiency gas turbines instead of less efficient gas engines. The other way – an increase of η by decreasing E_{in} – is usually neglected or used only in a minimal manner by minimizing the self-consumption of the auxiliary equipment, like sensors, mixer, etc.

In this paper - following a brief overview of PtM technology – a novel method will be presented to increase the total storage efficiency by increasing the conversion efficiency of PtM technology. This can be done by waste heat recovery from electrolysis and methanation by an Organic Rankine Cycle (ORC). A case study – using the data of an existing PtM installation – also will be shown, demonstrating the ability of this method to reach an approximately two percentage point increase in the storage efficiency.

2 Short overview of the PtM technology

By converting the excess electricity that is intermittently present in the power grid into gas that can be fed into the gas grid, PtM technology - although this can also be considered true for PtH technology – links the electricity and natural gas networks [14]. The process takes two steps, the production of H₂ by water electrolysis and the methanation of the produced H₂ by an external CO or CO₂ source (see Fig. 1). Although the resulting Substitute Natural Gas – also referred as Synthetic Natural Gas - (SNG) is suitable for feeding into the grid, the calorific value of the product gas may be lower than that of conventional natural gas. Namely, SNG does not contain long-chain hydrocarbons as conventional NG does. (NG contains methane above 80%, but ethane, propane, and butane as well, which increase the calorific value, and smaller amounts of the inert N₂ and CO₂, which reduce it [14]).

2.1 Water electrolysis

Electrolysis is an electrochemical process in which electrical energy (direct current) is converted into chemical energy. The redox reactions occur in the electrolytic cell, where cations are reduced on the surface of the negatively charged cathode, while anions are oxidized on the surface of the positively charged anode. The H_2 required for the PtM technology is produced by dissociation of H_2O , and the endothermic reaction is as follows:

$$H_2O_{(l)} + energy \leftrightarrow H_{2(g)} + \frac{1}{2}O_2$$
 (1)

The energy demand of the reaction is determined by the technology and depends on the temperature and pressure at which the reaction takes place [11]. According to Faraday's law, the H_2 produced during electrolysis is proportional to the magnitude of the electric current. Therefore, the technologies used aim to achieve the highest current density

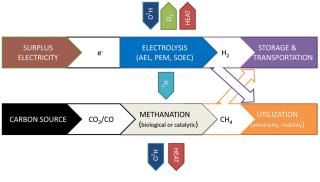


Fig. 1 Process flow of Power-to-Gas technology (adapted from [14])

possible for a given surface area of the electrolytic cell. The electrolysis efficiency is the ratio of the calorific value of H₂ produced, calculated as HHV_{H2} = 3.54 kWh/Nm³ or LHV_{H2} = 3 kWh/Nm³ depending on the application, to the electricity consumed during electrolysis [12].

Electrolyses in power-to-gas applications have special requirements [15]:

- high efficiency to avoid unnecessary energy losses;
- highly dynamic behavior to follow the fluctuating power input of renewables;
- very low minimal load to allow for stand-by mode with low energy consumption;
- ideally, the ability to produce hydrogen at elevated pressure to reduce energy demand and investment costs for compressors;
- long lifetime and low investment costs to allow for cheap hydrogen production.

Based on their utilized electrolyte [16], the three most common methods used for water electrolysis are alkaline electrolysis (AEL) with the following operating principle:

• Anode:

$$2OH^{-} \rightarrow 0.5O_2 + H_2O + 2e^{-};$$
 (2)

• Cathode:

$$2\mathrm{H}_{2}\mathrm{O} + 2\mathrm{e}^{-} \rightarrow \mathrm{H}_{2} + 2\mathrm{OH}^{-}; \qquad (3)$$

• Total reaction:

$$\mathrm{H}_{2}\mathrm{O} \rightarrow \mathrm{H}_{2} + 0.5\mathrm{O}_{2} \,. \tag{4}$$

Polymer electrolyte membrane electrolysis (PEM) with the following operating principle:

• Anode:

$$H_2O \rightarrow 2H^+ + 0.5O_2 + 2e^-;$$
 (5)

• Cathode:

$$2\mathrm{H}^{+} + 2\mathrm{e}^{-} \rightarrow \mathrm{H}_{2} + 2\mathrm{OH}^{-}; \qquad (6)$$

• Total reaction:

$$\mathrm{H}_{2}\mathrm{O} \rightarrow \mathrm{H}_{2} + 0.5\mathrm{O}_{2} \,. \tag{7}$$

And the high temperature (HTE) or solid oxide electrolysis (SOEC) with the working principle below:

• Anode:

$$O^{2^-} \to 0.5O_2 + 2e^-;$$
 (8)

• Cathode:

$$H_2O + 2e^- \to H_2 + O^{2-};$$
 (9)

• Total reaction:

$$H_2O \to H_2 + 0.5O_2$$
. (10)

Based on an extensive market survey, discussions with manufacturers, project reports and literature Buttler and Spliethoff [17] gave an overview on the current status of the different types of water electrolysis and summarized the key parameters of the state-of-the-art of water electrolysis technologies by covering the operation parameters, load flexibility, efficiency, available capacity, durability and even economic parameters.

AEL has a well-established technology; it is available for large plant sizes; uses non-noble catalysts, which keeps the costs relatively low and it has a long lifetime with long-term stability. However, AEL has low current density; low degree of purity, high maintenance costs because of the corrosive liquid electrolyte, and low partial load range, dynamics, and operational pressures. PEM, on the other hand, has high current densities, high voltage efficiency, high operating pressure, good partial load range, with high dynamics and compact system design. Yet, it is expensive, has a fast degradation, the components work in an acidic corrosive environment responsible for the low durability and high costs. The stacks are below the AEL range, and the technology did not reach the commercialization level of AEL. SOEL, operating under high pressure with possible integration of waste heat, has the highest efficiency (> 100%) among the three technologies, and just like AEL, it uses non-noble catalysts. The disadvantage of this technology is that the cells have limited long-term stability; it is not suited for fluctuating systems, is expensive, has a bulky system design, has relatively low durability, and there is no reliable cost information available as the technology is still in a laboratory stage [14, 18, 19].

As properties show, AEL is the most widely used water electrolysis method in the field of PtG at the moment. As SOEL is still in a laboratory stage, it is not expected to be a real alternative in water electrolysis to the other two technologies in the coming years. On the other hand, PEM can also be an important player in this field due to its fast response time, which makes it ideal for network regulation [20].

2.2 Biological methanation

Industrial-scale P2M technology can be divided into biological and catalytic methanations [21, 22]. While catalytic processes mainly use nickel and ruthenium-based catalysts [15] and take place at high temperatures, above 250 °C, biological methanation uses methanogenic microorganisms as biocatalysts [14] and takes place at much lower temperatures, usually below 70 °C, due to the thermophilic bacterial strains. In contrast to the catalytic process, where methanation efficiencies vary between 70 and 85% [23, 24], biological methanation can achieve efficiencies above 95% [21].

Unlike chemical methanation – which requires pure CO_2 or at least well-purified CO_2/CH_4 mixture for input – biological methanation can use various, even non- or minimally purified mixtures with CO_2/CH_4 content (like biogas or landfill gas). In this method, existing methane molecules can pass the methanation without any change; only the CO_2 molecules will be transformed. In the near future, biological methanation can be a viable method for biogas upgrading, overtaking presently used techniques, like water scrubbing [25].

In the presence of H_2 , microbes can convert the CO_2 in the biogas into CH_4 through their metabolism. When the CH_4 concentration of the resulting gas reaches 95–98%, the product gas is biomethane (bio CH_4) [26–28].

A distinction can be made between chemoautotrophic bacterial ([29–31]) strains, which obtain their energy chemically from inorganic sources, and photosynthetic bacterial strains ([26, 30, 32]), which receive their energy from light.

3 Increasing efficiency through waste heat recovery

The efficiency of electrical energy storage is the ratio of the electricity output to the electricity input. It is never 100%; there are always losses. An example from everyday life is the warming up of batteries (e.g., mobile phones) when charging. Heat is the loss in the form of dissipation which can be measured and felt. Losses may occur during recharge, when energy is stored in a standby state, or during discharge. Time-dependent losses in the standby state are often ignored; however, it is a crucial parameter of seasonal storage. These standby losses are low for PtM, making the technology competitive with battery or hydrogen storage for seasonal use [33, 34]. Considering a "semiideal" case (i.e., no standy-by losses), the total storage efficiency may be written as:

$$\eta = \frac{E_{out}}{E_{in}} = \frac{E_{out}}{E_{st}} \frac{E_{st}}{E_{in}} = \eta_{out} \eta_{in}$$
(11)

The storage efficiency (η) is the ratio of the energy output (E_{out}) to the energy input (E_{in}). If the recharge and discharge are sufficiently far apart in space and/or time, it is illustrative to split storage into two "half processes" with efficiency η_{out} (discharge) and η_{in} (recharge). In this case, an intermediate quantity appears in Eq. (11), the amount of energy stored in the storage. In the case of PtM, this is the energy content of the methane produced, which is in principle described by the higher heating value, in practice more by the lower heating value; the amount of η_{in} can then be treated as the efficiency of the bio-methane production.

The storage efficiency may be increased in two ways; the more common way is to maximize the recovery of the stored electricity, i.e., to extract as much as possible (E_{aut}) from a given amount of stored energy (E_{at}) . In the case of PtM technology, this means improving the process of recovering electricity from methane. One way is to recover some of the energy lost during conversion. Probably most methane (or natural gas) electricity conversion technologies use gas engines; the loss (up to 60-70%) then enters the surroundings at high temperature, as "good quality" waste heat. It is relatively easy to recover electricity from high-temperature waste heat; much research is being done on installing such recovery technologies on gas engines, and such equipment is already available. Examples include the Organic Rankine Cycle (ORC) described later [35].

Another way of increasing efficiency is to reduce the amount of electricity the PtM has to be charged with (E_{in}) for a given amount of stored energy (E_{i}) . The utilization of waste heat generated during recharge, especially in biological methanation where this heat has a relatively low temperature, has not been deployed so far. However, in recent years, the development of power generation equipment that can be applied to low-temperature heat sources has been improved significantly, making heat sources previously considered unusable, albeit with relatively low efficiency, usable. In PtM technology based on low-temperature electrolysis followed by biological methanation, waste heat is generated during both electrolysis and methanation; by generating electricity from this waste heat and feeding it back to the electrolyzer, the amount of electricity input can be reduced, thus increasing the recharge efficiency (η_{in}) and, through this, the overall storage efficiency, with the same stored energy (E_{st}) .

In the following, after presenting the Organic Rankine Cycle, the incremental gains achievable with this technology will be shown through a case study.

4 Organic Rankine Cycle

The Rankine cycle is a thermodynamic cycle that converts heat into mechanical work and, using a generator, into electricity. The single-component, two-phase working fluid of the cycle is water.

Due to the thermophysical properties of water, low-temperature energy conversion only appears at very low efficiency. Therefore, below the 350 °C temperature range, cycles with similar structures but different working fluids, so-called Organic Rankine Cycles (ORC), are used. Based on the slope of the saturated vapor line of the working fluid in a *T-s* diagram, a distinction can be made between wet, isentropic, and dry working fluids. This classification of working fluids is necessary because it significantly influences the structure and operation of the ORC. If the fluid was wet like water (Fig. 2 (a), (b) [36]), the medium entering the preheater (2, 3) after the pump (1, 2) would not only have to be vaporized (3, 4) but also superheated (4, 5), since in the case of expansion from a saturated vapor state (4, 6*) the moisture content at the expander outlet would increase

Generator

Condenser

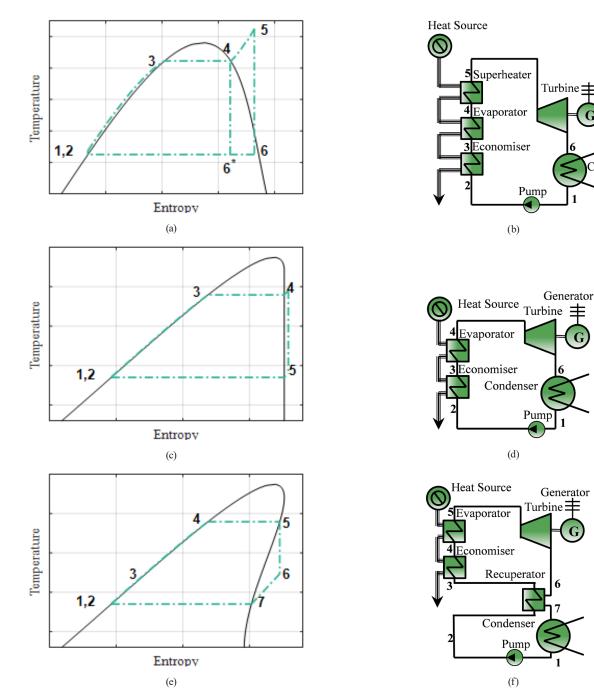


Fig. 2 T-s diagrams and their corresponding ORC layouts for wet (a), (b), isentropic (c), (d), and dry (e), (f) working fluids (adapted from [36])

to such an extent, that due to droplet erosion it could lead to a significant reduction in service life.

In contrast, with a dry working fluid (Fig. 2 (e), (f)), the saturated vapor (4, 5) exiting the evaporator can be expanded immediately, and no superheater is required since the properties of the working fluid will ensure that the fluid leaves the expander as superheated vapor (5, 6). However, the disadvantage of this solution is that if the superheated vapor were to reach the condenser directly, it would significantly increase its thermal load and reduce the cycle efficiency. Therefore, a recuperative heat exchanger (6, 7) is often used to preheat the working fluid (2, 3), leaving the pump before reaching the economizer. (More details can be seen in the Appendix.)

The ideal solution, however, is for the working fluid to be isentropic (Fig. 2 (c), (d)) since, in this case, the expansion starts from a saturated vapor state and ends in a saturated vapor one. Therefore, neither a superheater nor a recuperative heat exchanger is required for a reliable operation; thus, installation and maintenance costs will be lower.

Unfortunately, there is no perfectly isentropic working fluid, nor does ideal expansion exist. However, if the efficiency of the expander is taken into account when the working fluid is selected in a form that allows the expansion to start from and terminates in a nearly saturated vapor state, both the superheater and the recuperative heat exchanger become redundant, and a thermodynamically ideal solution is obtained with a layout capable of delivering maximum shaft power. For more details on the research on thermodynamically ideal working fluid selection taking into account the real expansion, see [37].

In the following, it will be shown how the conversion efficiency of a biological methanation-based alkaline electrolysis PtM technology can be increased through the Organic Rankine Cycle.

5 Case study

5.1 Introduction of the reference bio-methanation system

The biomethane production plant (BioCat) used as a reference in the study on the utilization of waste heat from bio-methanisation in ORC was erected between November 2015 and March 2016 at the BIOFOS wastewater treatment plant site in Avedøre, Denmark, Copenhagen area. The system, process flow diagram is shown in Fig. 3 [38], including a 9 m high BioCat reactor in a 12 m high frame,

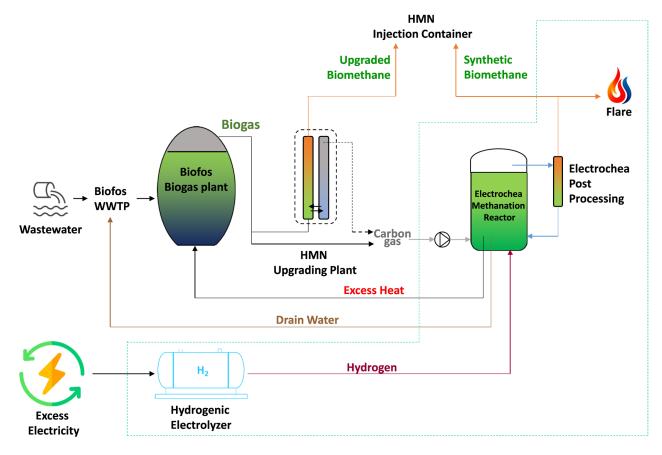


Fig. 3 General layout and integration of the ref. BioCat reactor (adapted from [38])

a 600 kW electrolyzer, and several containers for the utilities (water softening, power panels, instrument air, control-room, and gas analyzer).

The plant is designed to handle 50 Nm³ CO₂/h. The carbon source is either biogas from the anaerobic digestion of municipal sewage sludge or by-product gas from the purification of raw biogas before injection. The hydrogen for biological methanation is produced on-site by an electrolysis plant with a maximum production capacity of 110 Nm³ H₂/h. The gas leaving the biological reactor is post-treated to remove water, dust, and impurities as well as excess H₂ and/or unreacted CO₂. The residual gas from the post-treatment phases is recycled back to the reactor, while the mainstream is fed into the natural gas network. In the reference plant shown, the metabolic heat produced by the reactor was recycled through a water loop to Biofos to contribute to the heat demand for biogas production [38].

In this study it is assumed that the total waste heat from biomethane production is used in an Organic Rankine Cycle. Sufficiently high-temperature waste heat is generated at two locations. One is the metabolic heat generated in the reactor mentioned above. The other is the heat generated during electrolysis and dissipated by air. The energy balance of the reference bio-methanation system is shown in Fig. 4 [38]. Alkaline electrolysis and ex-situ biological methanation were applied in the investigated model. The temperatures at which waste heat were available for both locations were estimated based on data from the literature. The parameters of the waste heat recoverable in ORC are shown in Table 1.

A similar integrated system design based on the utilization of waste heat of the processes has been published by Wang et al. [39]. However, there are two crucial differences between the two systems. The system used by Wang et al. [39] is based on high-temperature SOEC electrolysis and high-temperature catalytic methanation. The produced high enthalpy - high temperature waste heat is easily utilizable. In the present case, the waste heat temperature is only around 60-70 °C, making it very difficult to utilize in power production The second difference is significant from the applications point of view: both electrolyzer types are relatively slow (compared to PEM electrolyzers), making them difficult to use for negative power regulation, required by systems with significant built-in photovoltaic capacity, but still, alkaline systems can be used in some extent for this purposes, while SOECtype electrolyzers should run permanently.

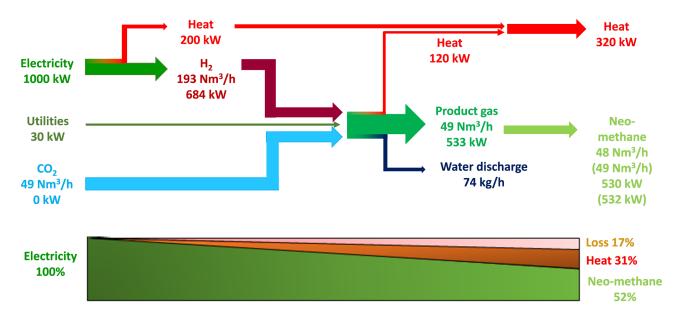


Fig. 4 Mass and Energy balance of the reference methanation system. The energetically unrecoverable loss (17%) of the summative energy rectangle (on the bottom) is not part of the Sankey diagram (on the top). (adapted from [38])

Table 1 Waste heat of the Biomethanation					
Location	Medium	Heatflow [kW]	Temperature [°C]	Pressure [bar]	Massflow [kg/s]
Electrolysis	air	200	70	30	39.498
Bio-reactor	water	120	65	1	5.736

5.2 Organic Rankine Cycle (ORC)

Four different options were analyzed when modeling the waste heat recovery with ORC. The case where a single ORC recovers all waste heat through series-connected heat exchangers was considered. Within this option, two concepts were modeled: a commercially available recuperative heat exchanger process and a tailor-suited layout capable of delivering maximum shaft work while considering the turbine's internal losses (expansion from saturated vapor to saturated vapor state). The other option was to consider separate ORCs installed next to the waste heat sources. In this case, the operation of two units was modelled twice, similar to the designs presented in the previous case - commercially available unit with recuperative heat exchanger and tailor-suited unit with maximum shaft work. In all cases, the coolant required to condense the ORC working fluid was assumed to be 20 °C air. After modelling, the results were compared.

5.2.1 Case I

All waste heat generated was recovered in one ORC through two heat exchangers connected in series. In the models, heat from the electrolyzer was utilized in the first heat exchanger, while heat from the bio-reactor was harvested in the second one.

Case I/a: The ORC was modeled based on an existing industrial design (Electratherm), which operates within the given temperature limits. Established on the information available on the system, the working fluid used in this case is R245fa (ElectraTherm Inc.). It also has to be mentioned that different ORC manufacturers use various fluids – some apply publicly available working fluids (such as R134a, N-pentane, Toluene, Ammonia, or other silicon oils), yet other companies prefer patented materials (such as Inducal[®]; Geocal[®] or Solkatherm[®]) –, but the greater majority operates with R245fa that justifies the choice. The expander is a twin-screw expander with an internal efficiency of 72% based on literature data [40]. The layout of the investigated model is shown on the left side of Fig. 5 and the process *T-s* diagram on the right.

The amount of heat recovered in the heat exchangers, the waste heat recovery rate, the cycle efficiency, and the power output are shown in Table 2.

The system has a power output of 16.98 kW at a 7.14% cycle efficiency, which increases the efficiency of the bio-methane production process by 1.65 percentage points.

Case I/b: In this case, the internal efficiency of the expander was also assumed to be 72%. The working fluid

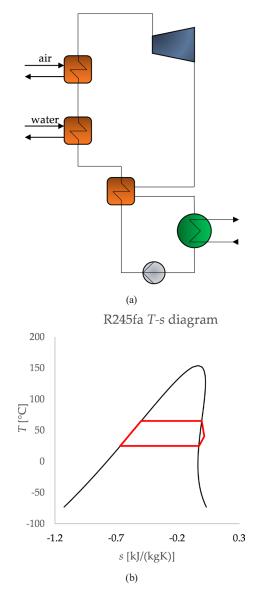


Fig. 5 (a) Modelling of waste heat recovery in the industrial ORC; (b) Process in the *T-s* diagram of R245fa

 Table 2 Energetic characteristics related to the industrial ORC

 (related to Fig. 5)

	(related	to Fig. 5)	
	Q, kW		P, kW
HTX1	199.15	T11	17.31
HTX2	38.63	P10	-0.33
Q	237.78	Q/Q_{sum}	74.30%
Q_{sum}	320.00	$\eta_{ m ORC}$	7.14%

was selected with the efficiency of the expander in consideration, resulting in the maximum shaft work at the given temperature pair – for the given heat source (70 °C) and heat sink (20 °C) temperature – requiring neither superheater nor recuperative heat exchanger. The working fluid used to model and fulfill the desired conditions is R134a. Detailed results on the optimal working fluid selection method can be found in [37]. Fig. 6 shows the layout of the tailor-suited ORC on the left side and the process in a T-s diagram on the right.

The system, designed with the optimal working fluid, has a cycle efficiency of 6.53% and a power output of 17.49 kW, which increases the efficiency (i.e., η_{in}) of bio-methane production by 1.7 percentage points. Table 3 shows the simulation results for the model.

5.2.2 Case II

The waste heat was recovered at the location of the source, so in this case, an ORC was installed at the electrolyzer and the bio-reactor separately. In the case of II/a, the

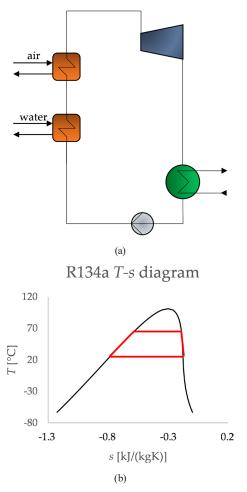


Fig. 6 (a) Modelling of waste heat recovery in the tailor-suited ORC;(b) Process in the *T-s* diagram of R134a

Table 3 Results of the tailor-suited ORC simulation with R134a
(related to Fig. 6)

(related to Fig. 0)				
	Q, kW		P, kW	
HTX1	199.15	T11	19.00	
HTX2	76.18	P10	-1.51	
Q	275.33	Q/Q_{sum}	86.04%	
Q_{sum}	320.00	$\eta_{ m ORC}$	6.35%	

industrial layout presented previously, and in the case of II/b, the structure providing the maximum shaft work for the different heat sources was investigated.

For the II/a case, as in the I/a, the working fluid is R245fa, the internal efficiency of the expanders is 72% and the systems include a recuperative heat exchanger. The modelled design, which is the same for both sources, is shown in Fig. 7.

The ORC connected to the electrolyzer has an efficiency of 7.11% and a power output of 14.22 kW using 200 kW of waste heat. The ORC using 120 kW of waste heat from the bio-reactor has an efficiency of 6.38% and a power output of 7.66 kW.

For the designs tested in II/b, it was no longer possible to use the working fluid as seen in I/b, as the maximum desired shaft work could not be reached using R134a for the 65 °C waste heat from the bioreactor. Therefore, the chosen working fluid becomes propane, as an expansion from saturated to near-saturated vapor state in an expander with an internal efficiency of 72% was achievable for 70 °C and 65 °C waste heat as well. The layout is shown in Fig. 8.

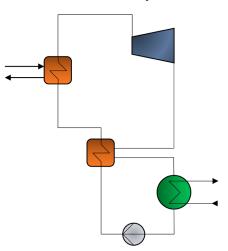


Fig. 7 Waste heat recovery at the location of the source, design of the industrial ORC

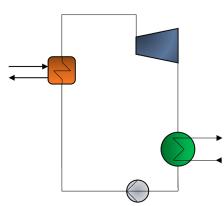


Fig. 8 Waste heat recovery at the location of the source, layout of the tailor-suited ORC

The ORC designed to use 200 kW of waste heat from the electrolyzer had a cycle efficiency of 6.23% and a power output of 12.45 kW. In the simulation, the ORC using 120 kW of waste heat at 65 °C had a cycle efficiency of 5.67% and a power output of 6.8 kW.

6 Results and discussion

The results obtained from the simulation are presented in Table 4.

From a purely technical point of view, it is preferable to convert the waste heat at the source location, as two ORC units can increase the electricity generated by 40%. The most favorable case from these points of view is II/a, with 21.88 kW of electricity, which can increase the efficiency of the PtM technology by 2.12 percentage points. Although most of the ORC systems are designed with higher capacity, there are specially designed small- and micro-ORC systems for this range [41].

From an economic point of view (especially from investment costs), however, only a solution where a single ORC recovers all waste heat through series-connected heat exchangers does worth contemplating. Thus, the most reasonable case is I/b. The choice of working fluid used here, optimized for the maximum shaft work, is not only technically more favorable than its industrial counterparts, but the unit is also cheaper, as it requires less equipment.

It would be favorable to give a complete cost-analysis, but being the biomethanation a fairly new technology, this estimation would be not adequately established; therefore, it is omitted.

It is also possible to use the ORC to drive the mixer of the methanation reactor and replace the electricity consumption of the mixer to satisfy its energy demand partially or entirely. The mixer of the bio-reactor can also be driven directly via coupling. In this case, no electricity conversion occurs, but the direct utilization of the ORC shaft work. This solution is cheaper (no generator is needed) and more efficient (even though generators have high efficiencies, it would still reduce the conversion efficiency

 Table 4 Simulation results for the recovery of waste heat from a PtM

plant in an ORC				
	Power	Initial	Efficiency	Efficiency
	of ORC	efficiency	of PtM	increase
	[kW]	of PtM	with ORC	[percentage point]
Case I/a.	16.98	51.46%	53.10%	1.65
Case I/b.	17.49	51.46%	53.15%	1.70
Case II/a.	21.88	51.46%	53.58%	2.12
Case II/b.	19.25	51.46%	53.33%	1.87

slightly). Comparing the data in Fig. 3 and Table 4, it can be seen that a significant amount of the 30 kW required for mixing (about 17–22 kW) could be covered by this source.

7 Summary

There is an increasing need for energy storage solutions with high storage capacity in the near future. One such solution, the so-called Power-to-Methane (PtM or P2M) technology, in which stored electricity is used to produce hydrogen by electrolysis and then methanized biochemically by adding CO_2 , was introduced. The main advantage of this technology is that the methane produced can be stored and used together with natural gas, but the disadvantage is its low storage efficiency.

Using data from an existing storage facility, it was shown how the recharge (and thus the overall storage) efficiency could be increased by converting the low-temperature waste heat from the water electrolysis and methanation plants back into electricity, using four different ORC-based configurations. The efficiency of converting electricity to bio-methane (i.e., the first part of the storage) increased by 1.65–2.12 percentage points depending on the configurations. If the conversion back to electricity remains unchanged, this increases overall efficiency with the same percentage.

CRediT author statement

Axel Groniewsky: Conceptualization, Methodology, Writing - Original Draft. **Réka Kustán**: Methodology, Investigation, Software. **Attila Imre**: Conceptualization, Writing - Review & Editing.

Acknowledgment

This work was performed in the frame of the 2020-3.1.1-ZFR-KVG-2020-00006 project, implemented with the support provided from the National Research, Development and Innovation Fund of Hungary, financed under the 2020-3.1.2-ZFR-KVG funding scheme. Part of the research reported in this paper and carried out at BME has been supported by the NRDI Fund (TKP2020 NC, Grant No. BME-NC) based on the charter of bolster issued by the NRDI Office under the auspices of the Ministry for Innovation and Technology. The work was also supported by the ÚNKP-21-3 and ÚNKP-21-5 New National Excellence Program of the Ministry for Innovation and Technology from the source of the National Research, Development and Innovation Fund and by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences.

References

- U.S. Energy Information Administration (EIA) "Annual Energy Outlook 2021", 2021. [online] Available at: www.eia.gov/aeo [Accessed: 25 November 2021]
- [2] He, W., King, M., Luo, X., Dooner, M., Li, D., Wang, J. "Technologies and economics of electric energy storages in power systems: Review and perspective", Advances in Applied Energy, 4, 100060, 2021. https://doi.org/10.1016/j.adapen.2021.100060
- [3] Das, C. K., Bass, O., Kothapalli, G., Mahmoud, T. S., Habibi, D. "Optimal placement of distributed energy storage systems in distribution networks using artificial bee colony algorithm", Applied Energy, 232, pp. 212–228, 2018.

https://doi.org/10.1016/j.apenergy.2018.07.100

- Jani, V., Abdi, H. "Optimal allocation of energy storage systems considering wind power uncertainty", Journal of Energy Storage, 20, pp. 244–253, 2018. https://doi.org/10.1016/j.est.2018.09.017
- [5] Das, C. K., Mahmoud, T. S., Bass, O., Muyeen, S. M., Kothapalli, G., Baniasadi, A., Mousavi, N. "Optimal sizing of a utility-scale energy storage system in transmission networks to improve frequency response", Journal of Energy Storage, 29, 101315, 2020. https://doi.org/10.1016/j.est.2020.101315
- [6] Pintér, G. "The potential role of power-to-gas technology connected to photovoltaic power plants in the Visegrad countries—A case study", Energies, 13(23), 6408, 2020. https://doi.org/10.3390/en13236408
- [7] Varone, A., Ferrari, M. "Power to liquid and power to gas: An option for the German *Energiewende*", Renewable and Sustainable Energy Reviews, 45, pp. 207–218, 2015. https://doi.org/10.1016/j.rser.2015.01.049
- [8] Sterner, M., Specht, M. "Power-to-gas and power-to-X—The history and results of developing a new storage concept", Energies, 14(20), 6594, 2021.

https://doi.org/10.3390/en14206594

- [9] Sterner, M., Stadler, I. "Handbook of Energy Storage: Demand, Technologies, Integration", Springer, 2019. ISBN 9783662555033
- [10] Blanco, H., Nijs, W., Ruf, J., Faaij, A. "Potential of Power-to-Methane in the EU energy transition to a low carbon system using cost optimization", Applied Energy, 232, pp. 323–340, 2018. https://doi.org/10.1016/j.apenergy.2018.08.027
- [11] Csedő, Z., Sinóros-Szabó, B., Zavarkó, M. "Seasonal energy storage potential assessment of WWTPs with power-to-methane technology", Energies, 13(18), 4973, 2020. https://doi.org/10.3390/en13184973
- [12] Lehner, M., Tichler, R., Steinmüller, H., Koppe, M. "The Powerto-Gas Concept", In: Power-to-Gas: Technology and Business Models, Springer, 2014, pp. 7–17. ISBN 978-3-319-03994-7 https://doi.org/10.1007/978-3-319-03995-4_2
- [13] Meylan, F. D., Piguet, F.-P., Erkman, S. "Power-to-gas through CO₂ methanation: Assessment of the carbon balance regarding EU directives", Journal of Energy Storage, 11, pp. 16–24, 2017. https://doi.org/10.1016/j.est.2016.12.005
- [14] Götz, M., Lefebvre, J., Mörs, F., McDaniel Koch, A., Graf, F., Bajohr, S., Reimert, R., Kolb, T. "Renewable Power-to-Gas: A technological and economic review", Renewable Energy, 85, pp. 1371–1390, 2016. https://doi.org/10.1016/j.renene.2015.07.066

- [15] Schiebahn, S., Grube, T., Robinius, M., Tietze, V., Kumar, B., Stolten, D. "Power to gas: Technological overview, systems analysis and economic assessment for a case study in Germany", International Journal of Hydrogen Energy, 40(12), pp. 4285–4294, 2015. https://doi.org/10.1016/j.ijhydene.2015.01.123
- [16] Mergel, J., Carmo, M., Fritz, D. "Status on Technologies for Hydrogen Production by Water Electrolysis", In: Stolten, D., Scherer, V. (eds.) Transition to Renewable Energy Systems, Wiley-VCH, 2013, pp. 423–450. ISBN 9783527332397 https://doi.org/10.1002/9783527673872.ch22
- [17] Buttler, A., Spliethoff, H. "Current status of water electrolysis for energy storage, grid balancing and sector coupling via power-togas and power-to-liquids: A review", Renewable and Sustainable Energy Reviews, 82(3), pp. 2440–2454, 2018. https://doi.org/10.1016/j.rser.2017.09.003
- [18] Carmo, M., Fritz, D. L., Mergel, J., Stolten, D. "A comprehensive review on PEM water electrolysis", International Journal of Hydrogen Energy, 38(12), pp. 4901–4934, 2013. https://doi.org/10.1016/j.ijhydene.2013.01.151
- [19] Laguna-Bercero, M. A. "Recent advances in high temperature electrolysis using solid oxide fuel cells: A review", Journal of Power Sources, 203, pp. 4–16, 2012. https://doi.org/10.1016/j.jpowsour.2011.12.019
- [20] Safari, F., Dincer, I. "Assessment and optimization of an integrated wind power system for hydrogen and methane production", Energy Conversion and Management, 177, pp. 693–703, 2018. https://doi.org/10.1016/j.enconman.2018.09.071
- [21] Zavarkó, M. "Energetikai diszruptív technológiafejlesztés által indukált változásvezetési modellek" (Change management models induced by disruptive energy technology development), PhD Dissertation, Corvinus University of Budapest, 2021. (in Hungarian)

https://doi.org/10.14267/phd.2022012

- [22] Lóránt, B., Tardy, G. M. "Current Status of Biological Biogas Upgrading Technologies", Periodica Polytechnica Chemical Engineering, 66(3), pp. 465–481, 2022. https://doi.org/10.3311/PPch.19537
- [23] Rönsch, S., Schneider, J., Matthischke, S., Schlüter, M., Götz, M., Lefebvre, J., Prabhakaran, P., Bajohr, S. "Review on methanation – From fundamentals to current projects", Fuel, 166, pp. 276–296, 2016. https://doi.org/10.1016/j.fuel.2015.10.111
- [24] Vannice, M. A. "The Catalytic Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen", Catalysis Reviews, 14(1), pp. 153–191, 1976. https://doi.org/10.1080/03602457608073410
- [25] Nashmin Elyasi, S., He, L., Tsapekos, P., Rafiee, S., Khoshnevisan, B., Carbajales-Dale, M., Mohtasebi, S. S., Liu, H., Angelidaki, I. "Could biological biogas upgrading be a sustainable substitution for water scrubbing technology? A case study in Denmark", Energy Conversion and Management, 245, 114550, 2021. https://doi.org/10.1016/j.enconman.2021.114550
- [26] Szuhaj, M., Bagi, Z., Kovács, L. K. "A "Power-to-Gas" és kapcsolódó biogáz tisztítási biotechnológiai eljárások" (Biogas purification technologies and the Power-to-Gas process), Energiagazdálkodás, 60(special issue), pp. 13–16, 2019. (in Hungarian)

- [27] Lóránt, B., László, K., Tardy, G. M. "Improving the Performance of Microbial Fuel Cells with Modified Carbon Aerogel Based Cathode Catalysts", Periodica Polytechnica Chemical Engineering, 66(1), pp. 1–9, 2022. https://doi.org/10.3311/PPch.18854
- [28] Lóránt, B., Gyalai-Korpos, M., Goryanin, I., Tardy, G. M. "Application of Air Cathode Microbial Fuel Cells for Energy Efficient Treatment of Dairy Wastewater", Periodica Polytechnica Chemical Engineering, 65(2), pp. 200–209, 2021. https://doi.org/10.3311/PPch.16695
- [29] Kougias, P. G., Treu, L., Benavente, D. P., Boe, K., Campanaro, S., Angelidaki, I. "*Ex-situ* biogas upgrading and enhancement in different reactor systems", Bioresource Technology, 225, pp. 429–437, 2017. https://doi.org/10.1016/j.biortech.2016.11.124
- [30] Angelidaki, I., Treu, L., Tsapekos, P., Luo, G., Campanaro, S., Wenzel, H., Kougias, P. G. "Biogas upgrading and utilization: Current status and perspectives", Biotechnology Advances, 36(2), pp. 452–466, 2018.
 - https://doi.org/10.1016/j.biotechadv.2018.01.011
- [31] Wu, L., Wei, W., Song, L., Woźniak-Karczewska, M., Chrzanowski, Ł., Ni, B.-J. "Upgrading biogas produced in anaerobic digestion: Biological removal and bioconversion of CO₂ in biogas", Renewable and Sustainable Energy Reviews, 150, 111448, 2021. https://doi.org/10.1016/j.rser.2021.111448
- [32] Muñoz, R., Meier, L., Diaz, I., Jeison, D. "A review on the state-ofthe-art of physical/chemical and biological technologies for biogas upgrading", Reviews in Environmental Science and Bio/Technology, 14(4), pp. 727–759, 2015.

https://doi.org/10.1007/s11157-015-9379-1

- [33] Kummer, K., Imre, A. R. "Seasonal and multi-seasonal energy storage by power-to-methane technology", Energies, 14(11), 3265, 2021. https://doi.org/10.3390/en14113265
- [34] Imre, A., Kummer, K. "Szezonális és hosszútávú energiatárolási lehetőségek" (Seasonal and long-term energy storage options), Energiagazdálkodás, 62(special issue), pp. 24–30, 2021. (in Hungarian)

Appendix

Thermodynamic scrutiny of the case studies was carried out based on the standard First-Law efficiency analysis. Considering Fig. 2 (e) and (f), which introduces the *T-s* diagram and ORC layout of a dry working fluid, the calculation is performed as follows:

• The energy balance of the evaporator is expressed as:

$$\dot{m}_{WF}\left(h_{5}-h_{4}\right)+\dot{Q}_{loss}=\dot{m}_{HS}\left(h_{evap,in}-h_{evap,out}\right),$$

where \dot{m}_{WF} and \dot{m}_{HS} are the mass flow rate of the heat source and working fluid, while h_5 , h_4 , $h_{evap,in}$, and $h_{evap,out}$ are the specific enthalpies of the working fluid and heat source fluid entering and leaving the evaporator, respectively. \dot{Q}_{loss} is the energy flow to the environment. Presuming that the heat exchanger is externally adiabatic, this value is zero.

- [35] Marami Milani, S., Khoshbakhti Saray, R., Najafi, M. "Exergoeconomic analysis of different power-cycle configurations driven by heat recovery of a gas engine", Energy Conversion and Management, 186, pp. 103–119, 2019. https://doi.org/10.1016/j.enconman.2019.02.030
- [36] Imre, A. R., Groniewsky, A. "Various Ways of Adiabatic Expansion in Organic Rankine Cycle (ORC) and in Trilateral Flash Cycle (TFC)", Zeitschrift für Physikalische Chemie, 233(4), pp. 577–594, 2019. https://doi.org/10.1515/zpch-2018-1292
- [37] Kustán, R., Imre, A. R., Groniewsky, A. "The effect of internal efficiency of expander on the working fluid selection", Refrigeration Science and Technology, 2020-July, pp. 351–357, 2020. https://doi.org/10.18462/iir.rankine.2020.1170
- [38] Lardon, L., Thorberg, D., Krosgaard, L. "WP3 Biogas valorization and efficient energy management: D 3.2: Technical and economic analysis of biological methanation", [pdf] Powerstep, 2018. Available at: http://www.powerstep.eu/system/files/generated/files/ resource/d3-2-technical-and-economic-analysis-of-biologicalmethanationdeliverable.pdf [Accessed: 02 November 2021]
- [39] Wang, L., Mian, A., de Sousa, L. C. R., Diethelm, S., Van Herle, J., Maréchal, F. "Integrated System Design of a Small-scale Power-to-Methane Demonstrator", Chemical Engineering Transactions, 61, pp. 1339–1344, 2017. https://doi.org/10.3303/CET1761221
- [40] Zhao, Y., Liu, G., Li, L., Yang, Q., Tang, B., Liu, Y. "Expansion devices for organic Rankine cycle (ORC) using in low temperature heat recovery: A review", Energy Conversion and Management, 199, 111944, 2019.

https://doi.org/10.1016/j.enconman.2019.111944

- [41] Gnutek, Z., Kolasiński, P. "The Application of Rotary Vane Expanders in Organic Rankine Cycle Systems—Thermodynamic Description and Experimental Results", Journal of Engineering for Gas Turbines and Power, 135(6), 061901, 2013. https://doi.org/10.1115/1.4023534
- [42] NIST "RefProp 9.1.", 2021. [online] Available at: https://www.nist. gov/srd/refprop [Accessed: 07 December 2021]
 - The same logic is applied to the economizer, recuperator, and condenser:

$$\begin{split} \dot{m}_{WF} \left(h_4 - h_3\right) + \dot{Q}_{loss} &= \dot{m}_{HS} \left(h_{eco,in} - h_{eco,out}\right), \\ \dot{m}_{WF} \left(h_3 - h_2\right) + \dot{Q}_{loss} &= \dot{m}_{WF} \left(h_6 - h_7\right), \\ \dot{m}_{WF} \left(h_7 - h_1\right) + \dot{Q}_{loss} &= \dot{m}_{cool} \left(h_{con,out} - h_{con,in}\right). \end{split}$$

• The heat flux between the heat source and the working fluid in the system is the sum of the heat absorbed by the evaporator and economizer:

$$\dot{Q}_{HS} = \dot{m}_{HS} \left(h_{evap,in} - h_{eco,out} \right).$$

• The system's net power (\dot{W}_{net}) is the difference between the power produced by the turbine (W_{turb}) and consumed by the pump (W_{pump}) :

$$\dot{W}_{net} = \dot{W}_{turb} - \dot{W}_{pump} \; . \label{eq:weak_net}$$

• The power consumption is calculated as

$$\dot{W}_{_{pump}}=\dot{m}_{_{WF}}\left(h_{2}-h_{1}
ight)=\dot{m}_{_{WF}}\left(h_{2,s}-h_{1}
ight)\!\!\left/\eta_{_{pump}}
ight,$$

while the produced power is specified as

$$\dot{W}_{turb} = \dot{m}_{WF} (h_5 - h_6) = \dot{m}_{WF} (h_5 - h_{6,s}) \eta_{turb}.$$

The η_{pump} and η_{turb} are the isentropic efficiency of the pump and turbine, respectively, while index *s* denote

adiabatic and reversible expansion (between states 5 and 6*s*) and compression (between states 1 and 2*s*).

• The thermal efficiency of the ORC system is expressed as:

$$\eta_I = \frac{\dot{W}_{net}}{\dot{Q}_{HS}} \, .$$

The thermodynamic properties of the working fluids were taken from the REFPROP database [42], the calculation was performed in CycleTempo heat-balance simulation software.