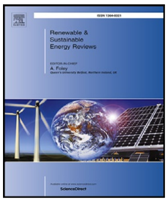
Renewable and Sustainable Energy Reviews 123 (2020) 109747

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser



Underground bio-methanation: Concept and potential

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ARTICLE INFO

Keywords:
Methanation
Underground storage
Energy storage
Conversion

ABSTRACT

As a major part of the energy turn around, the European Union and other countries are supporting the development of renewable energy technologies to decrease nuclear and fossil energy production. Therefore, efficient use of renewable energy resources is one challenge, as they are influenced by environmental conditions and hence, the intensity of resources such as wind or solar power fluctuates. To secure constant energy supply, suitable energy storage and conversion techniques are required. An upcoming solution is the utilization and storage of hydrogen or hydrogen-rich natural gas in porous formations in the underground. In the past, microbial methanation was observed as a side effect during these gas storage operations. The concept of underground bio-methanation arised, which uses the microbial metabolism to convert hydrogen and carbon dioxide into methane. The concept consists of injecting gaseous hydrogen and carbon dioxide into an underground structure during energy production peaks which are subsequently partly converted into methane. The resulting methane-rich gas mixture is withdrawn during high energy demand. The concept is comparable to engineered bio-reactors which are already locally integrated into the gas infrastructure. In both technologies, the conversion process of hydrogen into methane is driven by hydrogenotrophic methanogenic archaea present in the aqueous phase of the natural underground or above-ground engineered reactor. Nevertheless, the porous medium in the underground provides, compared to the engineered bio-reactors, a larger interface between the gas and aqueous phase caused by the enormous volume in the underground porous media. The following article summarizes the potential and concept of underground methanation and the current state of the art in terms of laboratory investigations and pilot tests. A short system potential analysis shows that an underground bio-reactor with a storage capacity of 850 Mio. Sm^3 could deliver methane to more than 600,000 households, based on a hydrogen production from renewable energies.

1. Motivation

In 2010 the European Union published its new energy and climate action strategy to improve the energy efficiency, increase the share of renewable energy sources and decrease the greenhouse gas emissions. In detail, the percentage of renewable energy sources should reach 20% until 2020 and 80%–95% until 2050, whereas the emissions should be reduced by 40% until 2030. As part of the European Union, the German government announced the concept “Energiewende” following the guideline from the European energy strategy. It includes the transformation of energy production from fossil fuels to renewable sources. The transition leads to extensive technology adaptations in various industry sectors. One challenging topic is the guarantee of a balanced energy supply for the consumers from fluctuating energy sources, as e.g. wind parks and solar power plants.

A sustainable option is the conversion from electrical energy into chemical energy via electrolysis. Chemical energy carriers in the form of gases can be stored in tanks or geological subsurface storages, for buffering the fluctuating production of electricity. The so-called Power-to-X technologies cover the conversion into different energy carriers such as fuel, methanol, and hydrogen (Power-to-Fuel, Power-to-Methanol, Power-to-Gas). Especially the production and refinement of “green” hydrogen as an energy carrier was studied in several engineering disciplines [1] and is nowadays linked to the Power-to-Gas technology (PtG).

Additional to the production of hydrogen via electrolysis and renewable energy, the conventional used natural gas reforming plants enable the production of “blue” hydrogen. In combination with carbon capture and hydrogen purification post-processing, it can lead to a carbon dioxide-lean hydrogen production for the energy supply system [2,3]. “Green” and “blue” hydrogen in combination can form the basis for a potential hydrogen energy economy [2].

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https://doi.org/10.1016/j.rser.2020.109747
Received 24 June 2019; Received in revised form 31 January 2020; Accepted 1 February 2020

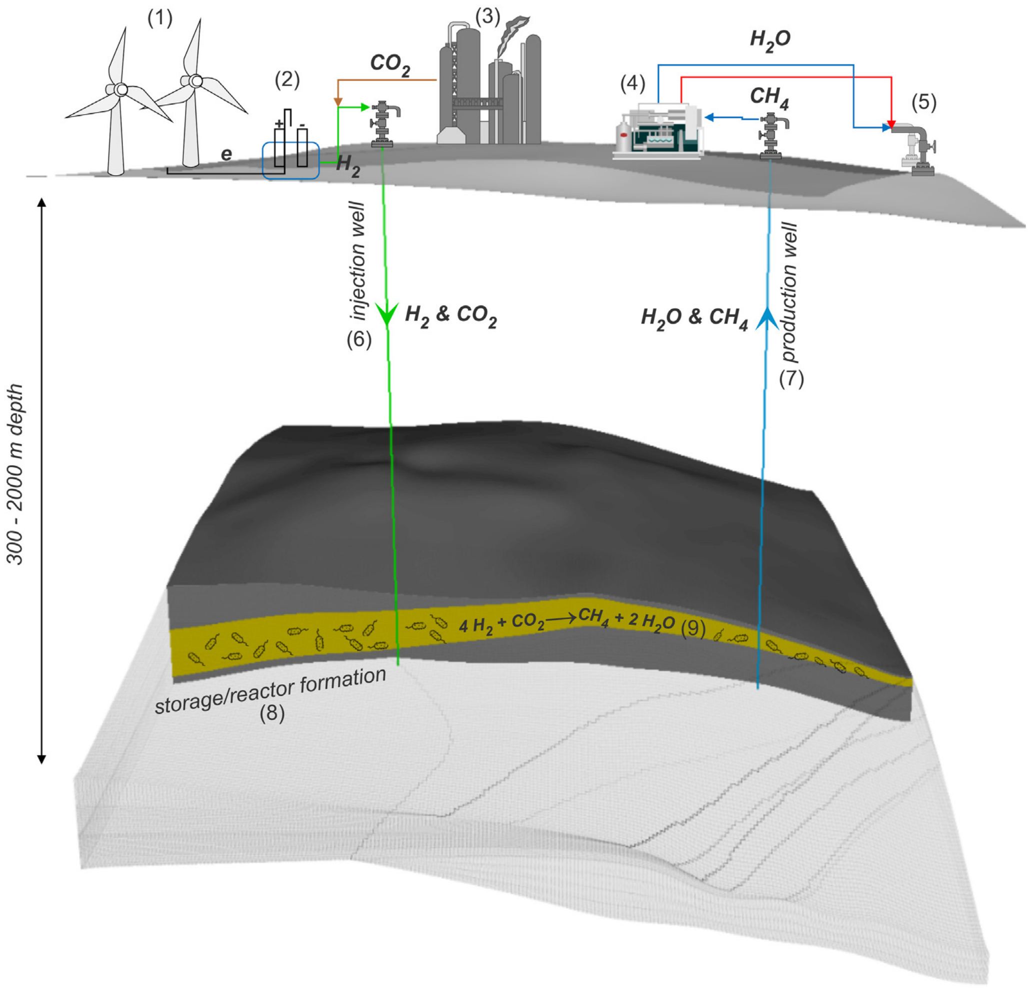


Fig. 1. The concept of a doublet system for underground bio-methanation.

Abbreviations

PtG	Power-to-Gas
UHS	Underground hydrogen storage
UMR	Underground methanation reactor
SMR	Steam methane reforming
ATR	Autothermal reforming

The possibility to store hydrogen in existing natural gas storages (UHS) and further the transportation via the gas supply network was investigated by companies and research institutes in the past years. The reservoir related studies show that besides complex hydrodynamics and well integrity questions the injection of hydrogen can intensify various microbial metabolisms in the underground [4], which compete for hydrogen as an energy source or nutrient. Four metabolisms were identified to play a significant role during the storage of hydrogen: the methanogenesis, acetogenesis, iron-reduction and fermentation [5–7]. Three of the stated metabolisms can be considered as negative side-effects, but the methanogenic metabolism can be used as an in-situ conversion process for an underground bio-reactor.

2. Concept

In the concept of an underground methanation reactor (UMR), hydrogen and carbon dioxide are injected into deep storage horizons via an injection well, sketched in Fig. 1 and originally proposed by Panfilov et al. [8]. A proportion of the injected mixture is converted into methane and water during the metabolism of methanogenic archaea.

The technical concept of underground bio-methanation is directly related to the technology of underground natural gas storage or underground hydrogen storage. The gas is injected (6 in Fig. 1) in the porous formation (8 in Fig. 1). Instead of using only the storage capacity of the porous underground, the conversion takes place in-situ (9 in Fig. 1). The gas subsequently consisting of methane and hydrogen can be withdrawn by a production well (7 in Fig. 1) and further processed.

A suitable location of an underground bio-reactor depends on two main criteria: the geological environment and the above-ground installations. The potential geological environment is described in detail in Section 3.

In order to implement an underground bio-reactor, three criteria have to be fulfilled on the surface, excluding operation facilities like compressors, wellbores, and separators. First, the deliverability and transport of gases to the reactor and away have to be in place. The hydrogen production via electrolysis (2 in Fig. 1) is nowadays mostly implemented near the electrical power generation, meaning near wind and solar farms (1 in Fig. 1). The “green” hydrogen has to be transported to the underground reactors. Further, the produced “green” methane or gas mixture from the reactor has to be processed and delivered via pipelines (5 in Fig. 1) to the consumers.

A review of the state of the art and outcome of essential research projects should help to conclude the potential of underground methanation, criteria for an underground bio-reactor as well as conclude the need for additional research.

3. Reservoir requirements and potential in the subsurface

The underground bio-reactor uses a deep porous geological reservoir as a reactor, where the conversion of stored hydrogen and carbon dioxide into methane is directly related to gas storage operations.

Two storage types are technologically feasible [9]: storage in leached salt caverns for short term storage and working gas volumes up to 138 Mio. Sm^3 (in Germany) [10] and storage in naturally formed porous structures for long term storage and enormous working gas volumes (up to 4.4 Bil. Sm^3 in Germany) [10]. In both technologies, two types of gases have to be distinguished. The working gas is the usable amount of gas in the storage, whereas the cushion gas belongs permanently to the inventory and secures an adequate minimum pressure throughout the withdrawal period. The storage sites are often operated with multiple production and injection wells.

From a geological point of view, the underground bio-methanation requires various conditions, which are summarized in the following list:

- First, a porous rock is required. This rock should have a porosity of more than 10%, which secures an enormous reactor volume of up to 3 Bil. Sm^3. Siliciclastic rocks, for example sandstone, are the favorable rock types, because the reactions between minerals, mostly quartz, and injected gas are limited [11]. The origins of siliciclastic rocks are mostly sedimentary rocks, which were formed and processed by transport, weathering and the diagenesis processes.
- Besides the suitable rock type, the storage requires a geological trap, e.g. an anticline (left part in Fig. 2) or a fault (right part in Fig. 2), to prohibit vertical and horizontal gas migration. Above the reactor formation, an impermeable cap rock should seal the formation. Shales and salts like halite are suitable cap rocks. The sealing capacity of the rock type further depends on its capillary threshold pressure. Exceeding the threshold pressure plus the initial reservoir pressure can cause leakage of gas through the upper formation. The suitable structures and the trapping principles are shown in Fig. 2. An additional trapping mechanism that limits especially lateral migration of gas is the occurrence of sedimentary unconformities or discordances [12].
- The pores in the rock should be connected. The conductivity (permeability) influences the movement of the gas towards and away from the well. Low permeability (below 10 mD) can cause injectivity problems for the injection well and less nutrient supply for microbes.
- A certain water saturation (minimum 10%) in the porous rock is crucial because the formation water is the region where microbes grow. Dried out zones in reservoirs provide no space for microbes to live and, consequently, no conversion into methane.
- The salt content inside the formation water could be an inhibitor for the growth of microbes. The magnitude of salt content is related to the geological history of the location [13]. Based on the data, shown in Section 4, the salt content in the formation water should not exceed 150 g/l.
- A temperature between 30–70 °C is favorable. The temperature in a reservoir can be calculated by the geothermal gradient, which is typically assumed to be 3 °C per 100 m [14] in Germany. Locally this gradient can be different and could lead to extremely high temperatures [15]. The temperature can limit or inhibit the growth of methanogenic archaea.

Two porous reservoir types are suitable for the methanation: Aquifers and depleted gas and oil reservoirs. They differ mainly in their initial pore-filling fluid. Aquifers are filled with brine, whereas depleted hydrocarbon reservoirs can contain oil, water, and gas. Depleted reservoirs, in contrast to aquifer storages, provide proven sealing capability for natural gas, because the hydrocarbons were trapped in the formation for a geological period.

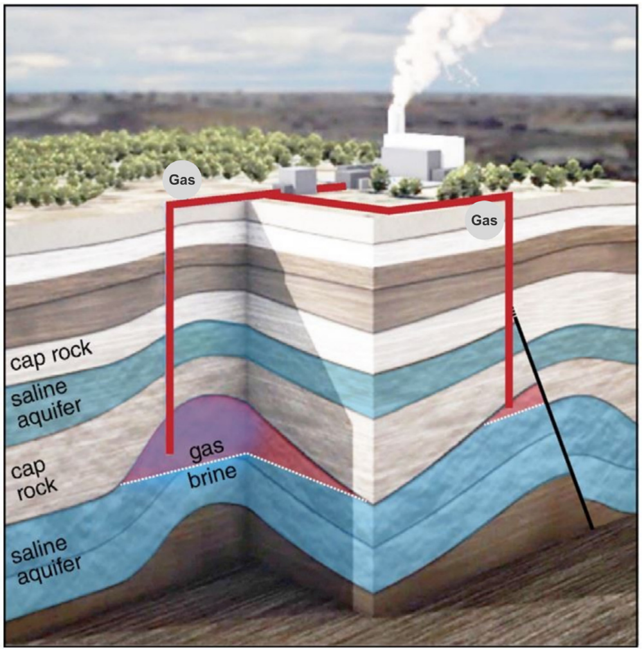


Fig. 2. The concept of geological gas storage in porous reservoirs; trapping principles apply to aquifer and deplete reservoir storage: Anticline trapping (left part) and faults (right part). Modified after [12].

Pressure is not a critical factor for the methanation process but is important for the operation of the reactor. A higher initial reservoir pressure impedes the operation of an underground reactor, because the injection pressure required to inject gas is higher. Pressure and temperature are related to the depth of the formation. A deeper formation results in a higher temperature and pressure. Further, porous reservoirs are often found in a deeper formation. Therefore the depth of an underground methanation reactor should be between 300 m and 2000 m.

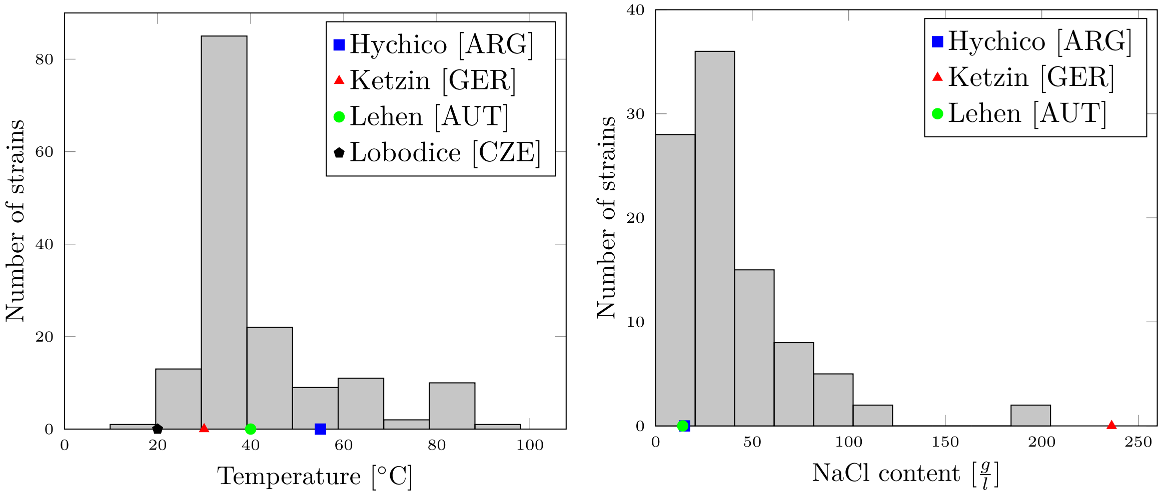
4. Microbial potential in the subsurface

Underground methanation is achievable through the utilization of microbes in the reservoir. These specific microbe strains can transform carbon dioxide through their metabolic reaction into the desired methane gas. The expression “microbe” is purposely chosen over the term bacteria because all methane producing microbes belong to the archaea domain. A distinctive archaea domain feature is that its representatives are often referred to as the extreme survivors in the community of small organisms [16].

Solely, the methanogenic archaea are capable of synthesizing methane. Based on their biological classification the relevant microbes are referred to as methanogens for simplicity. Methanogens are a wide spread class, and their living environment ranges from the subsurface to the intestinal tract of animals, insects or humans. The methanogens are organized into four different classes with multiple families with 161 individual methanogen strains. Current known classes of methanogens are the Methanobacteria, Methanococci, Methanopyri and Methanomicrobia. The largest class is the Methanomicrobia class with 90 individual strains stands in contrast to the single strain Methanopyri class. Second largest class is the Methanobacteria with 55 individual strains. Further, there are 15 individual species of Methanococci [17].

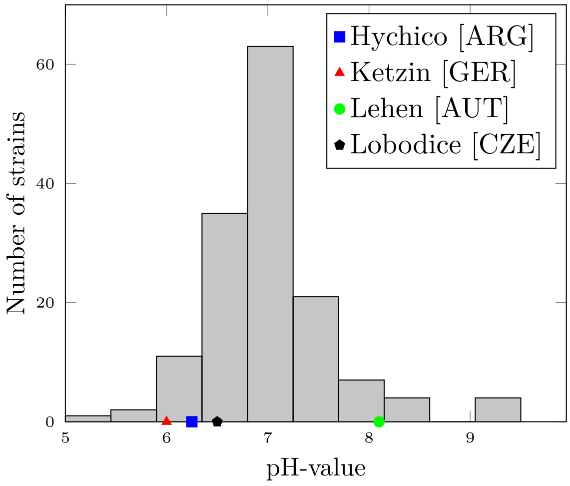
During the hydrogenotrophic methanation process carbon dioxide is transformed into methane and water. The reaction equation of methanation is described the subsequent way:

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O - 135\frac{kJ}{mol(CH_4)} \tag{1}$$



(a) Optimal temperature distribution [°C]

(b) Critical NaCl content distribution [$\frac{g}{l}$]



(c) Optimal pH-value distribution

Fig. 3. Histograms of bacteria species and their dependency on conditions.

The reaction is a strong exothermic conversion process. Technically the reaction is used nowadays in nickel catalysis with temperature up to 300 °C [1]. In the case of underground bio-methanation the archaea act as a bio-catalyst. The archaea are present in the water phase of the reservoir and use the dissolved carbon dioxide as a carbon source and electrons from the dissolved hydrogen for their metabolisms. Various methanogens can utilize other electron donors such as formate or acetate to produce methane gas. Some strains are unable to utilize hydrogen as an electron donor and are specialized on other electron donors. A number of methanogens require other grow conditions such as a minimum NaCl concentration or the presence of certain vitamins, yeast extract or rumen fluid [18], which are either already present in the reservoir fluid or can be injected and mixed with the reservoir fluid.

Methanogen strains possess variable attributes regarding their pH-value, temperature, salinity, and nutritional preferences. Differences occur between the separate biological classes but are also prevalent between related family strains. Adaptation to the predominant living conditions is a requirement of growth. This is because in an underground environment temperature, salinity, pH-value and nutrition concentration can be extreme, thereby restricting microbial growth. Exceeding the maximum feasible conditions of a strain decelerates the cell creation process and as a result the methane production. To further investigate underground methanation feasibility an awareness of methanogens temperature, salinity, pH-value and nutritional preference is important [19].

Regarding temperature preferences the methanogens are spread through all categories. Methanogens live and thrive in a mesophilic, thermophilic and hyperthermophilic and even psychrophilic environment. The optimal temperature is the temperature where potentially the greatest growth rate occurs. The lowest optimal living temperature know for a methanogen is 15 °C by the methanomicrobia class strain Methanogenium frigidum. The highest known optimal temperature is 98 °C by the methanopyri class strain Methanopyrus kandleri. Microbes can exceed their optimal temperature towards a maximum growth temperature. The highest maximum growth temperature is 110 °C by the methanopyrus kandleri strain. There are nine strains that prefer a hyperthermophile environment and 14 strains which prefer psychrophilic environment. There are a considerable number of methanogens that favor elevated temperatures above 60 °C, which demonstrates the temperature resilience [20]. The distribution of the classes is summarized in Fig. 3a.

Fig. 3b displays the critical NaCl concentration values for 96 different methanogen strains. The critical NaCl concentration of various methanogens is not available. Two known strains, which are extremely halophile are the Methanocalculus halotolerans and natrophilus. Further, 16 strains survive under halophilic conditions, which shows that specific methanogens have a considerable salinity tolerance. Whereas the halophilic methanogens are spread over the mesophilic, thermophilic and hyperthermophile temperature range both extremely halophile strains dwell in a mesophilic environment. Demonstrating

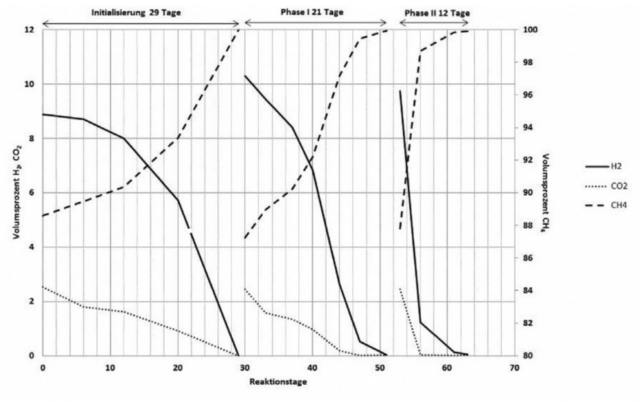


Fig. 4. Measured metabolic rate in bio-reactors. Dotted line shows the CO_2 concentration, straight line the H_2 concentration and the dashed line the CH_4 concentration. [22].

that elevated resistance against a chosen property does not automatically equate other property resistances. Contrary to the salinity resistant strains there are nine fragile strains which endure low amount of salinity. The variety shows the diversity between the strains and demonstrates that a strain suited for industrial purposes must possess a diversity of attributes [21].

Concerning the pH-level, which is illustrated in Fig. 3c, the methanogens mostly prefer neutral conditions with a small acidic inclination of around pH 6.5 to 7. There are few strains that grow optimally under acidic conditions of pH 5. Three to four strains favor alkaline conditions with an optimal pH value of 9 to 9.5. The critical pH-value range spreads for the methanogens majority from pH 5 to 8.5. There are a few strains that can endure higher alkaline conditions with an critical pH-value of 10 and a selected few strains that can endure acidic conditions of 4. The strains enduring the elevated alkaline conditions are the Methanobrevibacter gottschalkii, millerae, and olleyae, the Methanospirillum hungatei, and stamsii, the Methanosalsum natronophilum and zhilinae. Further, Methanocalculus alkaliphilus and halophilusare are the two extremely halophilic methanogen strains. Regarding the extreme acidic range, the Methanobacterium espanolae, and palustre, the Methanocaldococcus bathoardescens, the Methanococcus aeolicus, the Methanothermococcus okinawensis, the Methanoregula boonei, the Methanosarcina baltica and soligelidi are known.

An example of the microbial potential in the reservoir can be concluded from the Underground Sun.Storage project [4]. The microbial consortium inside the formation water was analyzed and tested for the methanation in high-pressure bio-reactors on the laboratory scale. In the following, two analysis were performed during the experiments: gas composition and microbial consortium. All experiments were conducted under near reservoir conditions (45 °C and 45 bar). Additional to the formation water, rock cores with the similar mineralogical composition were added to the batch reactor. Methane, admixed with hydrogen and carbon dioxide was used as the feed gas.

The hydrogen and carbon dioxide fraction decreases over time, while the methane concentration increased slightly. In comparison, no changes in hydrogen concentration were observed in the abiotic reactors. Besides the gas composition changes, which were measured in the field test (Section 7.1), the microbial consortium indicates a significant shift. The initial concentration of methanogens was below 5% and the population was dominated by proteobacteria and chloroflexi bacteria. At the end of the experiments, the proportion of methanogens archaea grows to more than 75%. The compositional changes during experiments, shown in Fig. 4, demonstrate the potential of the conversion process.

DNA and RNA investigations of the formation brine before and after the field test show a similar shift in the microbial consortium over time. Initially, the consortium was also dominated by fermentation bacteria species, which include the sulfate-reducers, and a small percentage of methanogenic archaea. The test during the production period indicates an increased population of methanogenic archaea up to a share of 60%, whereas the fermentation species quantity stayed constant. Due to the lack of measured H_2S impurities in the reservoir and the constant population of sulfate-reducers, the dominant metabolism was concluded to be methanogenesis.

5. Related research projects

Numerous research projects have been launched during the last decades which consider the use of subsurface structures related to renewable energies (e.g. ANGUS+ [23], H2STORE [11], SACRE [24], HyINTEGER [25], Underground Sun.Storage [4]) and greenhouse gas control (e.g. CO2CRC [26], CO2SINK [27], Sleipner Project [28], CLEAN [29]). In particular these projects concern the cyclic storage of energy in the form of hydrogen, methane, compressed air or heat or the permanent disposal of carbon dioxide. It was shown that microbiological interactions could become relevant when the stored medium alters the living conditions or acts as electron donor or acceptor for the microbial metabolism [6,7,30]. The impact of microbiological processes during the underground storage of hydrogen was investigated by laboratory experiments [4,31] and by mathematical and numerical modeling [6,8,32–39]. In addition, the microbiological processes during geological CO_2 storage were studied [27,30,40–43]. However, the significant contrast to the intended microbiological methanation is the fact that during these applications microbiological interaction are side-effects and potentially limited by the availability of a carbon source or an electron acceptor [7]. A very special case might be the underground storage of natural gas with admixed hydrogen. Natural gas, depending on its origin, can contain small percentages of CO_2 so that the stored gas mixture contains H_2 and CO_2. In such a case the conditions are similar to the concept of underground methanation.

Only two projects are known to the authors which focus on the injection of H_2 and CO_2 mixtures with the aim to induce microbiological methanation.

5.1. *Underground Sun.Conversion [44]*

The project “Underground Sun.Conversion” headed by the Austrian company RAG Austria AG started in 2017 as follow-up project of “Underground Sun.Storage”. During “Underground Sun.Storage” it was demonstrated in a field test that the storage of natural gas with admixed 10% H_2 is technically feasible. The microbiological transformation of hydrogen into methane observed during this project led to the idea for the new project, see also Section 7.1. The consortium consisting of Austrian companies, universities and research institutions intends to investigate the technology of underground microbiological methanation by laboratory experiments, simulations and a field test. In the first stage it is planned to inject a H_2-CO_2-natural gas mixture into a sandstone reservoir in a depth of 1000 m. After a certain retention time the gas will be withdrawn by the same well. Pressure, temperature and gas composition will be observed. In the second stage it is planned to drill an additional well in order to run the microbiological conversion process with one injection and one production well in a cyclic way. The planned completion date is 2021.

5.2. *Hychico-BRGM pilot project [45]*

Th Argentinean company Hychico S.A. started an hydrogen energy program some years ago. In the first stage they have build a hydrogen plant producing 120 Sm^3/h of H_2 by using energy from a nearby wind park. In 2010 they begun to study the possibility to store the hydrogen in a depleted gas reservoir. In the following years they made a field test by operating different hydrogen-natural gas storage cycles using a reservoir in a depth of 815 m. During this test the H_2 concentration in the reservoir reached up to 10%. The storage cycles were accompanied by analysis of changes in the reservoir properties and gas composition. Similar to the field test performed by RAG they have observed that some of the stored hydrogen was converted into methane. In the next stage they are studying the possibility of intended underground microbiological methanation. In cooperation with the French Geological Survey (BRGM) the planned investigations include biological characterization, laboratory experiments and field tests. They reported that the first results indicate favorable conditions for the process of microbiological methanation.

6. Analogy to town gas storage

Storages of town gas were the first experiences with hydrogen-rich gas injection into the subsurface. The different storages showed partly extreme reservoir behavior due to microbial activity, which were similar to an UMR. Town gas (also referred to as manufactured gas) is a fuel gas produced by the gasification of coal which was used from the middle of the 19th century until the 1990s for lightning, cooking, and heating. The main components of town gas are H_2 (25% to 60%), CH_4 (10% to 30%), N_2 (7% to 30%), and $CO+CO_2$ (12% to 20%) [12,46]. It also contains some minor concentrations of O_2, H_2S, and other hydrocarbons [12,46]. For the balance of seasonal fluctuations in demand underground storages for town gas were operated in Germany, France, the Czech Republic, Poland, and the USA beginning in the middle of the 20th century. Similar to the present natural gas storages, town gas was stored in salt caverns, aquifers and depleted gas and oil reservoirs. During the approximately 40 years of experience some abnormalities as for example changes in the gas composition, volume losses, temperature increase, permeability reduction, H_2S generation, acidification, and increased corrosion at subsurface installations were observed [7,47–49]. Chemical reactions and especially microbiological reactions were interpreted as the main cause for the behavior but could not definitively be confirmed in all cases. The fact that these abnormalities were not observed at all town gas storages and some of them were operated without any problems shows that the behavior depends strongly on the prevailing conditions in the reservoir [49]. Town gas contains some additional reactive components (CO and O_2) so that the experiences cannot be directly transferred to the technology of underground methanation [49]. Nevertheless, the experiences are essential because the stored gas contained H_2 and CO_2. Furthermore, it demonstrates that high impure gas streams can affect the geological/well bore integrity, reservoir properties and stimulate not desirable metabolisms. A few extreme examples are summarized in the following subsections.

6.1. Lobodice (Czech Republic)

The most prominent example from the literature is the town gas storage in an anticline aquifer structure near Lobodice, Czech Republic. It was reported that during a storage cycle of seven months the CH_4 concentration increased from 22% to 40% while the CO, CO_2 and H_2 concentrations decreased from 9%, 12% and 54% to 3%, 9% and 37%, respectively [50]. In addition, a volume (or storage pressure) loss of 10%–20% was observed [50,51]. Smigan et al. [50] analyzed fluid samples from the storage formation which showed populations of methanogenic microorganisms with a density in the order of 10^3 to 10^4 cells per ml. Cultivation experiments proved the potential to convert H_2 and CO_2 into CH_4. The conclusion that microbiological reactions were responsible for the compositional changes was confirmed by carbon-isotope analysis of the storage gas which confirmed the biological origin of a part of the methane [51]. In this former town gas storage the process of underground bio-methanation was clearly observed which confirms the possibility for this technology.

6.2. Ketzin (Germany)

In the town gas storage Ketzin gas losses in the order of 1.5-fold of the working gas volume were observed between 1964 and 1985 [12]. In addition, small changes in the gas composition of up to 3%–4% and a temperature increase of 30–40 °C was reported [7,12]. The trends in the compositional change are not clear but overall an increase in H_2, CO_2 and CH_4 and a decrease in CO was observed [12]. Changes in permeability and increased corrosion of the underground installations were also reported. Microbiological and chemical processes have been concluded as reasons but the behavior was not completely understood [12].

6.3. Beynes (France)

In contrast to the previous examples no unexpected behavior or problems were observed in the Beynes field, France [12,52]. The 400 m deep aquifer structure was used to store town gas from 1956 until 1974. It was reported that no gas losses, compositional changes or any other problems occurred [52].

7. Comparison to underground storage of hydrogen

The underground hydrogen storage technique is the basis for the underground methanation reactor because the methanogenic metabolism requires a significant amount of hydrogen in the reservoir. The technical feasibility of UHS in caverns and porous media storages was proven recently by various pilot projects, which are summarized in the following section.

The cyclic storage of pure hydrogen or hydrogen-rich natural gas mixtures in the subsurface is similar to conventional natural gas storage. Hydrogen is either mixed with natural gas or injected purely with the help of compressors through (an) injection well(s) into the underground. The methanation potential differs between pure hydrogen injection, where a direct carbon source is missing, and hydrogen enriched natural gas, where the required carbon source (e.g., carbon monoxide, carbon dioxide) can be present.

During the field test in Austria [4], which is the only one with accessible results, changes in the gas composition were observed. For the field test performed in Argentina by Hychico [45] no results in terms of gas compositions or microbial analysis were published, but in the follow-on project "green" methane first methanogen reactions were confirmed in the lab [53]. The experience with hydrogen storage in caverns shows the low potential for underground methanation, caused by the harsh living condition and the limited gas/water phase contact in the cavern. Porous media, in comparison, provide a favorable structure for microbes. Nevertheless, the effect of salt content or temperature in the reservoir can reduce the growth of microbes.

7.1. Lehen (Austria)[4]

During the Underground Sun.Storage project, the former gas field "Lehen-002" in Upper Austria was converted into an underground hydrogen storage test facility. Over three months 10% of hydrogen, produced form electrolysis, was mixed with the natural gas stream and injected via a single well into the reservoir. During the shut-in period (four months) and the withdrawal period (three months) the composition of withdrawn gas changed compared to the injected gas. The methane concentration increased up to 96% [54], whereas the hydrogen concentration decreases to 7% and the carbon dioxide quantity reduces from 0.2% to 0.06%. The methanogenic metabolism is difficult to identify clearly by only analyzing the concentration of withdrawn H_2 and CH_4 because it is superimposed by gas mixing effects between the injected and initial gas. An extrapolation of the hydrogen concentration trend in the last third of the production phase leads to the assumptions that 4%–5% of the injected hydrogen diffused into the

Table 1
Comparison of underground bio-reactor and underground hydrogen storage [6,54,55].

Criteria	Technology	
	Underground bio-reactor	Underground hydrogen storage
Aim	Conversion and storage	Storage
Working gas	CH_4 and 4:1 H_2/CO_2	H_2 pure or admixed
Storage type (s)	Porous rock	Porous rock or salt cavern
Depth [m]	<2000	<3500
Favorable temperature [°C]	≤65	–
Water saturation [%]	>10	<20
Porosity [%]	>10	>10
Permeability [mD]	>50	>50
Salinity $[\frac{g}{l}]$	<150	–
Surface facilities	H_2/CH_4 gas grid, compressor, filter membrane	

initial natural gas. However, one clear identifier for metabolism is the CO_2 concentration which is low concentrated in the injected and initial gas and consequently very sensitive to the compositional changes. An estimation of the converted CO_2, taking into account the injected volume, leads to the conclusion, that 3% of the injected hydrogen was consumed by methanogenic microbes. The conclusion was supported by a methane isotope analyzes of the storage gas [4,44,54].

In contrast to the observations, see Section 6, during town gas storage, no increased temperature or significant pressure losses in the reservoir were recorded [4,44,54]. Based on the assumption that 3% of the injected hydrogen was converted into methane, the metabolic rate for the complete reactor volume can be estimated roughly. The reactor volume is equal to the total gas volume of the reservoir, which was reported to be 6 Mio. Sm^3 [4,44,54]. The metabolic rate for methane is $1.6559 * 10^{-9} \frac{\mathrm{mol}}{\mathrm{s} * \mathrm{Sm}^3}$. The results of the pilot test, clearly indicate the methanation potential inside the subsurface. In order to conclude the differences of an underground bio-reactor and underground storage of hydrogen, the criteria derived in Sections 2 and 3 were compared.

As shown in Table 1, the technologies are similar in most of the chosen criteria, but the intention of injecting gas into the underground differs. Underground hydrogen storage acts as buffer for the renewable energy production, whereas underground methanation combines storage of energy and conversion into methane at one place. Also, the handling on the surface is similar. In general, the gas mixture produced from the production well is further processed by different surface facilities (4 in Fig. 1). One suitable solution to separate the hydrogen from the methane is a membrane technique. For instance, membranes out of polyamide-fiber should be technically feasible to separate methane and aliphatic hydrocarbons from a gas mixture [4].

8. Differentiation to engineered bio-reactors

In a full hydrogen chain, the UMR replaces the bio-methanation as a conversion part. In order to conclude the overall potential of underground methanation in a hydrogen-based economy, the comparable techniques of engineered bio-reactors are reviewed.

Two main bio-methanation concepts already exist in the PtG technology without subsurface storage: the in-situ methanation inside a digester and the ex-situ methanation in a separate reactor [1]. Both concepts use microorganisms' metabolisms to produce methane, but the pathway differs.

In the commonly used method of the anaerobic digester, the biomass is hydrolyzed to monomers, which are converted further into acetate, carbon dioxide, and hydrogen. Afterwards, additional hydrogen is injected into the digester and the acetate and carbon dioxide are transformed into methane by acetoclastic and hydrogenotrophic microorganisms. The ex-situ methanation uses a separate reactor behind the digester. A 4:1 ratio of hydrogen and carbon dioxide is injected in this reactor, where hydrogentrophic methanogens (archaea) produce methane.

The dominating limiting factor for the methane production rate in both technologies is the gas/liquid mass transfer, especially of hydrogen [56,57]. To overcome this limitation, different types of reactors were proposed to improve the mixing: the continuous stirred-tank reactor (CSTR), fixed-bed, trickle-bed, and membrane reactor [57]. The CSTR uses mechanical agitation and stirring to enhance the mass transfer. This mechanical input requires a significant amount of extra electrical energy and affects the overall energy efficiency. In terms of working principles, the trickled-bed, fixed-bet and membrane reactors are similar to an underground porous medium. In the reactors, the liquid covered surface area of the porous medium provides a large gas–liquid interface area, which leads to an increased mass transfer rate and consequently an improved methane reaction rate [58]. The porosity, which is between 60%–70% in the membrane and trickle-bed reactors [59,60], depends on the packing density and used material for the bed. However, the artificial porous medium in the reactors requires higher gas rates and can cause pore-blocking by the produced biomass [58]. In comparison, the underground provides a natural porous structure with enormous pore volumes and flow capability. However, pore blocking by the microbes is far more critical, because the pore throat size and porosity is much smaller compared to engineered bio-reactors.

Additional to low mass transfer rates between the fluid phases, the anaerobe digester requires a permanently adapted H_2 injection, to balance the carbon dioxide production in the reactor, which leads consequently to complex automation and controlling requirements [61] whereas the ex-situ reactors work with a pre-defined gas stream (4:1 ratio H_2/CO_2). In the UMR such an automation system or predefined gas stream is not required, because the reservoir acts as storage and improves the mixing of the gaseous components. However, the 4:1 ratio should be ensured at least in average over a longer time period.

Due to the step-wise conversion process in bio-reactors, the in-situ methanation is operated with undefined cultures, whereas in the ex-situ process also enriched pure cultures from biogas plants can be used. In terms of additional operation requirements, both technologies are flexible in working temperature, which is a matter of the used cultures, pressure, which partly effects the gas–liquid mass transfer, and impurities. Regarding the PtG full chain, the methanation inside reactors cannot be operated as dynamically as the electrolysis. Therefore, a hydrogen storage for the bio-methanation reactors is required to compensate the fluctuating hydrogen production [1]. The hydrogen storage is named to be the critical part of the chain because it is costly and influences the energetic efficiency [1], whereas the UMR combines the storage of hydrogen and its conversion in the porous medium. The requirements of an UMR depend on the reservoir conditions and injector/producer configuration. However, the critical point is not the operation rather the presence and the suitable living conditions for methanogenic archaea inside the reservoir.

Nevertheless, surface bio-methanation is still a locally suitable solution to produce methane. It further can be used as a potential significant carbon dioxide source, which is often missing in the PtG technology. In combination with the carbon capture technology, it could deliver a high amount of gaseous carbon dioxide, which is an essential input for underground bio-methanation.

9. Simulation, designs and patents

First design ideas and one patent application exist for underground bio-methanation. In principle, the required gas mixture can be injected by huff and puff or by using different wells for injection and production.

The patent application [22], handed in by the RAG Austria AG in 2016, describes a gas cycle of a hydrogen/carbon-dioxide/methane gas mixture by using two wells. The injected methane concentration should be at minimum 10% and hydrogen and carbon dioxide should be admixed in a 4:1 ratio. Where a suitable microbial consortium is not present, it can be added artificially into the underground from other locations. Furthermore, the distance between the wells should be estimated in such a way that not more thane 18% carbon dioxide is produced (at the production well) [22]. The patent application describes a gas cycle process with different concentrations in the gas stream. However, operation requirements are mainly based on laboratory work.

In the study of Hogeweg et al. [55], a well-doublet system was simulated, where H_2 and CO_2 were continuously injected in a 4:1 ratio admixed to nitrogen. The artificial reservoir, which has the dimension 1500 m × 1500 m × 5 m, was initialized with a gas saturation of 89% consisting of 97% nitrogen. The operating pressure was 130 bar. Different injection rates (Case 1: $q_{inj} = 10$ mol/s, Case 2: $q_{inj} = 25$ mol/s, Case 3: $q_{inj} = 75$ mol/s) were simulated to optimize the methane concentration in the production well, which was located 500 m away from the injector.

The simulations show an increase of methane in the withdrawn gas [55] up to 14% after 20 years for the medium injection rate, shown in Fig. 5b. Whereas the higher and lower injection rates give less methane production. The microorganisms start growing in the vicinity of the injector. With ongoing cycling of hydrogen and carbon dioxide, the population increases in the reservoir, see Fig. 5a.

In the simulation study, the metabolic reaction rates are highly depending on the population kinetic parameters describing the microbial activity in the bio-reactive mathematical model. The study and patent application show that the overall design of a UMR is specific for each reservoir and microbial consortia.

The capturing and recovery efficiency of the produced methane is a problem at two points in the system: in the reservoir and on the surface. Gas recovery from porous structures is mostly due to pressure depletion, where some gas is trapped in the outer area of the reservoir or mixed with the initial fluid (gas or water). The cycling or recovery of gas from the underground is a well-known technique in the oil and gas industry [28]. However, the loss of gas is a common storage problem and not directly related to an underground bio-reactor. For implementing an underground bio-reactor, the storage/reservoir has to be transformed into a reactor by injecting hydrogen and carbon dioxide to maintain the operating pressure. Thereby, the gas losses mentioned before are already compensated. Under operation, no cycled gas should be lost due to mixing or trapping. Nevertheless, the systems loses energy due to the metabolism of the microbes. In fact, all carbons are recovered (carbon dioxide or methane), but some energy is converted to heat. The energy efficiency of the complete reaction is ca. 83% [62].

10. Potential for the energy system

The potential of the underground bio-reactor depends on the expansion of renewable energy producers and the production of hydrogen from electrolysis. Several studies were published, concluding the contribution of Power-to-X technologies in the future energy system with a focus on Europe or Germany. The main missing part for a Power-to-X system is suitable storages. Further, the storage capacity is depending on the share of renewable energies in energy production. Most studies show that the fluctuation in the energy system with a renewable energy share of 67% can be compensated by the extension of the electric grid in Europe [63,64]. The critical share of renewable energies is stated to be above 67%. With further increase in renewable energy production, the need for chemical storage rises. The required storage capacity is depending on the calculated residual power of the energy system [63]. The residual power capacity can only be estimated or simulated because the share of renewable energies nowadays is not exceeding 30% (in Germany).

Different studies try to predict the residual power and resulting required storage capacity. Where Henning et al. [64] concluded a surplus of 103 TWh for the electrolysis, taking into account the complete energy production system with 78% of renewable energy production, Zapf et al. [63] estimated a required gas volume after the electrolysis of 7.32 TWh for 80% renewable energy and 49.52 TWh for 100% in Germany. The efficiency of the electrolysis is stated to be between 65%–80%. Therefore, the produced hydrogen volume ranges from 8 to 80 TWh, which is equal to 2.6 – 26 Bil. Sm^3.

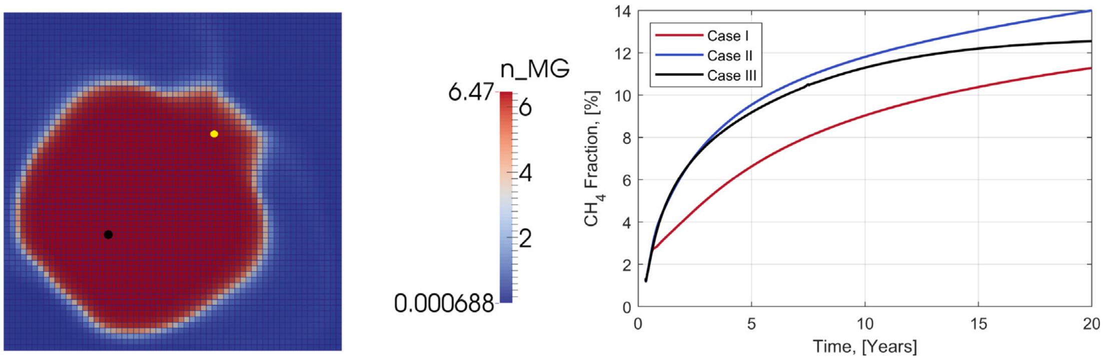
As the underground methanation only appears in porous structures, whose capacity in Germany is 9.1 Mio. Sm^3, not all of the produced hydrogen volume could be stored in the current existing storages. However, the potential for porous storages in Europe is enormous. As the oil and gas production is declining in Europe, the depleted reservoirs, onshore and offshore, could be used for storing and converting hydrogen. The working gas capacity in the following calculation is assumed to be 850 Mio. Sm^3, which is typical for a porous structure in Germany. 80% of the working gas is hydrogen, whereas 20% (170 Mio. Sm^3) is carbon dioxide. As four moles of hydrogen are converted into one mole of methane, the produced methane volume is 160 Mio. Sm^3, under the assumption that the working gas volume is replaced completely over one year. This could deliver enough methane for ca. 630,000 households (heating only). If additional hydrogen is recovered as a by-product, it could be re-injected or delivered to the gas power plant (efficiency 60%) [63].

11. Conclusion and potential

The underground bio-methanation was up to now only observed as a side-effect during hydrogen-rich gas storage operations but may be also interesting for the development of a designed underground bioreactor system (UMR) in porous underground structures. The advantage of the UMR compared to the engineered bio-methanation reactors is the enormous reactor volume combined with storage, which both are stated to be critical aspects in the bio-methanation process chain [1,65]. Additionally, the underground provides a natural porous structure with a residual unsterile brine saturation and allows a high operating pressure (depending on the depth of the reservoir), which both favor the gas–liquid mass transfer rate similar to the trickle-bed reactors. At the same time, the UMR has the same flexibility in terms of impurities, microbial cultures and loads. Critical design factors for the UMR are the appearance and living conditions of the microbial population. High salinity in the brine and high temperatures can edge the growth of the methanogenic microorganisms.

During the methanation process, the biomass in the aqueous phase of the reservoir increases significantly and can cause bio-clogging effects. Anyway, the growth of biomass in the pores could have an impact on the hydrodynamics of the reservoir, but the impact on the working gas capacity could be neglectable. It has to be mentioned that the water production of the microbes during the methanation metabolism could cause a reduction of the gas capacity due to an increase in water saturation. This theoretical effect has to be proven.

At the current state of the technology and research, no efficiency factor or methane production rate for comparison to other methanation concepts can be concluded, because the behavior and population kinetics of methanogens in a porous structure are not fully understood yet. This is essential to improve the existing mathematical model, which then can be used to predict the performance of an UMR. Based on simulations and prediction, methane production rates and efficiency, as well as revenues, could be calculated. Besides lack of microbial conversion rates, adverse effects as concurrences inside the microbial consortium (e.g. sulfate-reducers), well integrity (e.g., hydrogen embrittlement) problems and pore-blocking, have to be investigated [11]. However, the performed simulation studies for UHS and well-doublet systems show, the UMR concept holds a high potential for the conversion of hydrogen during the transition in the energy sector. The capability of storage and conversion at the same place could help to centralize the energy from the locally installed electrolysis facilities. Further, the UMR can potentially be an important conversion part in a hydrogen-based energy sector and a lean-carbon circular economy, where carbon capture from carbon-rich industries and "green/blue" hydrogen production is



(a) *Number of methanogenic microorganisms after 20 years simulation with* $q_{inj} = 25 mol/s$ (b) *Methane concentration in the producer for different injection rates*

Fig. 5. Results of well-doublet simulation including microbial methanation (black/yellow dot: producer/injector) [55].

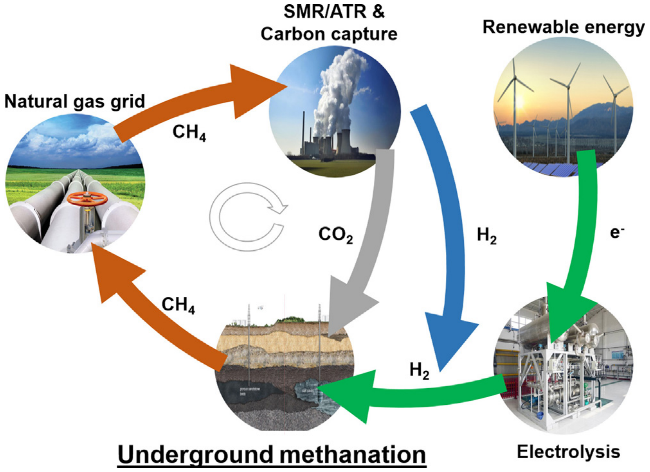


Fig. 6. The concept of a low carbon dioxide circle with underground methanation.

combined [66]. The so-called carbon circular economy is sketched in Fig. 6.

The produced bio-syngas or “green” methane from the UMR is added into the existing gas infrastructure and used in gas-power facilities or chemical industries. Up to now, there are no regulations or economical frameworks for hydrogen or “green” methane production. The German gas law for instance allows the injection of 10% hydrogen in the gas grid and the admixing of bio-gas (“green” methane), whereas other countries in the European Union are not permitting hydrogen content in pipelines [67]. Nevertheless, hydrogen or “green” methane is an important factor for the future [67]. The frameworks for the gases have to be developed in the upcoming years, to create a basis for economical hydrogen and “green” methane industries.

The current ongoing research projects “Underground Sun.Conversion” and “Hychico” are first excellent opportunities to study the potential for underground methanation on a longer time and field scale and conclude the role of the UMR.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This publication is based upon work supported and financed by the Clausthal University of Technology, project Catalytic and microbial methanation as basis for sustainable energy storage (CliMb).

The authors acknowledge the support of the Research Center for Energy Storage Technologies Goslar (Forschungszentrum Energiespeichertechnologien) for the present study.

Funding

This research received no external funding.

References

[1] Götz M, Lefebvre J, Mörs F, Koch AM, Graf F, Bajohr S, Reimert R, Kolb T. Renewable power-to-gas: A technological and economic review. Renew Energy 2016;85:1371–90. http://dx.doi.org/10.1016/j.renene.2015.07.066, URL http://www.sciencedirect.com/science/article/pii/S0960148115301610.
[2] van Cappellen L, Croezen H, Rooijers F. Feasibility study into blue hydrogen - Technical, economic and sustainability analysis. CE Delft; 2018.
[3] Jakobsen D, Åtland V. Concepts for large scale hydrogenproduction. Norwegian University of Sience and Technology; 2016.
[4] Bauer S. Underground Sun.Storage Final Report, https://www.underground-sun-storage.at, Vienna, 2017.
[5] Cord-Ruwisch R, Seitz H-J, Conrad R. The capacity of hydrogenotrophic anaerobic bacteria to compete for traces of hydrogen depends on the redox potential of the terminal electron acceptor. Arch Microbiol 1988;149(4):350–7. http://dx.doi.org/10.1007/BF00411655.
[6] Hagemann B. Numerical and analytical modeling of gas mixing and bio-reactive transport during underground hydrogen storage. (Ph.D. thesis), Université de Lorraine, Clausthal University of Technology; 2017.
[7] Wagner M, Ballerstedt H. Influence of bio-methane and hydrogen on the microbiology of underground gas storage. literature study; Einfluss von Biogas und Wasserstoff auf die Mikrobiologie in Untertagegasspeichern. Literaturstudie. 2013.
[8] Panfilov M, Reitenbach V, Ganzer L. Self-organization and shock waves in underground methanation reactors and hydrogen storages. Environ Earth Sci 2016;75(4):313.
[9] Stone HBJ, Veldhuis I, Richardson RN. Underground hydrogen storage in the UK. Geol Soc Lond Spec Publ 2009;313(1):217–26. http://dx.doi.org/10.1144/SP313.13, arXiv:http://sp.lyellcollection.org/content/313/1/217.full.pdf. URL http://sp.lyellcollection.org/content/313/1/217.
[10] Untertage-Gasspeicherung in Deutschland. Erdöl-Erdgas-Kohle 2018;134(11):410–7.
[11] Ganzer L, Reitenbach V, Pudlo D, Panfilov M, Albrecht D, Gaupp R, et al. The H2STORE project-experimental and numerical simulation approach to investigate processes in underground hydrogen reservoir storage. In: EAGE annual conference & exhibition incorporating SPE Europec. Society of Petroleum Engineers; 2013.
[12] Liebscher A, Wackerl J, Streibel m. Geologic storage of hydrogen – fundamental, processing, and projects. In: Hydrogen science and engineering, 2 Volume set: Materials, processes, systems, and technology, Vol. 1. John Wiley & Sons; 2016.

[13] Lahner L, Lorenz W. Lagerstätten von mineralischen und Energierohstoffen. Leibniz-Institut für Länderkunde; 2001.

[14] Agemar T, Weber J, Schulz R. Deep geothermal energy production in Germany. MPI-energies; 2014.

[15] Gupta H, Roy S. Chapter 4 - Geothermal systems and resources. In: Gupta H, Roy S, editors. Geothermal energy. Amsterdam: Elsevier; 2007, p. 49–59. http://dx.doi.org/10.1016/B978-044452875-9/50004-6, URL http://www.sciencedirect.com/science/article/pii/B9780444528759500046.

[16] Chmiel H, editor. Bioprozesstechnik. 3rd ed.. Heidelberg: Spektrum Akademischer Verlag; 2011, http://dx.doi.org/10.1007/978-3-8274-2477-8, URL http://site.ebrary.com/lib/alltitles/docDetail.action?docID=10494116.

[17] Zehnder AJB, Wuhrmann K. Physiology of a methanobacterium strain az. Arch Microbiol 1977;111(3):199–205. http://dx.doi.org/10.1007/BF00549357.

[18] Moser A. Bioprocess technology. [Place of publication not identified]: Springer-Verlag New York; 2012.

[19] O'Flaherty V, Mahony T, O'Kennedy R, Colleran E. Effect of ph on growth kinetics and sulphide toxicity thresholds of a range of methanogenic, syntrophic and sulphate-reducing bacteria. Process Biochem 1998;33(5):555–69. http://dx.doi.org/10.1016/S0032-9592(98)00018-1.

[20] Schügerl K, Bellgardt K-H, editors. Bioreaction engineering: Modeling and control ; with 70 tables. Berlin: Springer; 2000.

[21] Archer DB, Powell GE. Dependence of the specific growth rate of methanogenic mutualistic cocultures on the methanogen. Arch Microbiol 1985;141(2):133–7. http://dx.doi.org/10.1007/BF00423273.

[22] Mitteregger M, Bauer S, Loibner AP, Schritter J, Gubik A, Backes D, Pichler M, Komm R, Brandstätter-Scherr K. Method for the hydrogenotrophic methanogenesis of h2 and co2 into ch4, no. EP3280807A1, European Patent Office.

[23] Bauer S, Dahmke A, Kolditz O. Subsurface energy storage: geological storage of renewable energy—capacities, induced effects and implications. Springer; 2017.

[24] Agency TFNR. Projet SACRE. 2019, Website, http://www.agence-nationale-recherche.fr/Project-ANR-10-STKE-0006.

[25] Henkel S, Pudlo D, Heubeck C. Laboratory experiments for safe underground hydrogen/energy storage in depleted natural gas reservoirs. In: Fourth sustainable earth sciences conference. 2017.

[26] Sharma S, Cook P, Berly T, Lees M. The CO2CRC otway project: Overcoming challenges from planning to execution of australia's first ccs project. Energy Procedia 2009;1(1):1965–72.

[27] Würdemann H, Möller F, Kühn M, Heidug W, Christensen NP, Borm G, Schilling FR, Group C, et al. CO2SINK—From Site characterisation and risk assessment to monitoring and verification: One year of operational experience with the field laboratory for co2 storage at ketzin, Germany. Int J Greenh Gas Control 2010;4(6):938–51.

[28] Hermanrud C, Andresen T, Eiken O, Hansen H, Janbu A, Lippard J, Bolås HN, Simmenes TH, Teige GMG, Østmo S. Storage of co2 in saline aquifers–lessons learned from 10 years of injection into the utsira formation in the sleipner area. Energy Procedia 2009;1(1):1997–2004.

[29] Kühn M, Münch U. CLEAN: CO2 large-scale enhanced gas recovery in the altmark natural gas field-geotechnologien science report, no. 19. Springer Science & Business Media; 2012.

[30] Morozova D, Zettlitzer M, Let D, Würdemann H, et al. Monitoring of the microbial community composition in deep subsurface saline aquifers during co2 storage in ketzin, Germany. Energy Procedia 2011;4:4362–70.

[31] Würdemann H, Halm H, Lerm S, Kleyböcker A. Verbund-Forschungsvorhaben H2STORE: Untersuchung der geohydraulischen, mineralogischen, geochemischen und biogenen Wechselwirkungen bei der Untertage-Speicherung von H2 in konvertierten Gaslagerstätten : Teilprojekt 4- Mikrobiologie. Potsdam: Helmholtz-Zentrum Potsdam Deutsches GeoForschungsZentrum GFZ; 2016.

[32] Ebigbo A, Golfier F, Quintard M. A coupled, pore-scale model for methanogenic microbial activity in underground hydrogen storage. Adv Water Resour 2013;61:74–85.

[33] Panfilov M. Underground and pipeline hydrogen storage. In: Compendium of hydrogen energy. Elsevier; 2016, p. 91–115.

[34] Panfilov M, Gravier G, Fillacier S. Underground storage of h2 and h2-co2-ch4 mixtures. In: ECMOR X-10th European conference on the mathematics of oil recovery. 2006.

[35] Hagemann B, Rasoulzadeh M, Panfilov M, Ganzer L, Reitenbach V. Hydrogenization of underground storage of natural gas. Comput Geosci 2016;20(3):595–606.

[36] Hagemann B, Rasoulzadeh M, Panfilov M, Ganzer L, Reitenbach V. Hydrogenization of underground storage of natural gas-impact of hydrogen on bio-chemical transformations of stored gas. In: ECMOR XIV-14th European conference on the mathematics of oil recovery. 2014.

[37] Hemme C, van Berk W. Hydrogeochemical modeling to identify potential risks of underground hydrogen storage in depleted gas fields. Appl Sci 2018;8(11):2282.

[38] Pfeiffer W, Graupner B, Bauer S. The coupled non-isothermal, multiphase-multicomponent flow and reactive transport simulator opengeosys–eclipse for porous media gas storage. Environ Earth Sci 2016;75(20):1347.

[39] Hagemann B, Ganzer L, Panfilov M. Field scale modeling of bio-reactions during underground hydrogen storage. In: ECMOR XVI-16th European conference on the mathematics of oil recovery. 2018.

[40] Morozova D, Wandrey M, Alawi M, Zimmer M, Vieth A, Zettlitzer M, Würdemann H, Group C, et al. Monitoring of the microbial community composition in saline aquifers during co2 storage by fluorescence in situ hybridisation. Int J Greenh Gas Control 2010;4(6):981–9.

[41] Kuramochi Y, Fu Q, Kobayashi H, Ikarashi M, Wakayama T, Kawaguchi H, Vilcaez J, Maeda H, Sato K. Electromethanogenic co2 conversion by subsurface-reservoir microorganisms. Energy Procedia 2013;37:7014–20.

[42] Wandrey M, Pellizari L, Zettlitzer M, Würdemann H. Microbial community and inorganic fluid analysis during co2 storage within the frame of co2sink–long-term experiments under in situ conditions. Energy Procedia 2011;4:3651–7.

[43] West JM, McKinley IG, Palumbo-Roe B, Rochelle CA. Potential impact of CO2 storage on subsurface microbial ecosystems and implications for groundwater quality. Energy Procedia 2011;4:3163–70.

[44] Bauer S. Underground sun conversion - erneubares erdgas zur speicherung von sonne und wind. Vienna: RAG Austria AG; 2018.

[45] Pérez A, Pérez E, Dupraz S, Bolcich J. Patagonia wind-hydrogen project: Underground storage and methanation. In: 21st World hydrogen energy conference 2016. 2016.

[46] Stolzenburg K, Hamelmann R, Wietschel M, Genoese F, Michaelis J, Lehmann J, Miege A, Krause S, Sponholz C, Donadei S, et al. Integration von Wind-Wasserstoff-Systemen in das Energiesystem. In: Analysis on behalf of Nationale Organisation Wasserstoff-und Brennstoffzellentechnologie GmbH (NOW). 2014.

[47] Gniese C, Bombach P, Rakoczy J, Hoth N, Schlömann M, Richnow H-H, Krüger M. Relevance of deep-subsurface microbiology for underground gas storage and geothermal energy production. In: Geobiotechnology II. Springer; 2013, p. 95–121.

[48] Letcher TM, Law R, Reay D. Storing energy: with special reference to renewable energy sources. Elsevier Oxford; 2016.

[49] Müller-Syring G, Henel M, Köppel W, Mlaker H, Sterner M, Höcher T. Entwicklung von modularen Konzepten zur Erzeugung, Speicherung und Einspeisung von Wasserstoff und Methan ins Erdgasnetz. In: Deutscher Verein des Gas-und Wasserfaches eV. 2013.

[50] Smigáň P, Greksak M, Kozankova J, Buzek F, Onderka V, Wolf I. Methanogenic bacteria as a key factor involved in changes of town gas stored in an underground reservoir. FEMS Microbiol Ecol 1990;6(3):221–4.

[51] Buzek F, Onderka V, Vančura P, Wolf I. Carbon isotope study of methane production in a town gas storage reservoir. Fuel 1994;73(5):747–52.

[52] Foh S, Novil M, Rockar E, Randolph P. Underground hydrogen storage final report. New York, USA: Brookhaven National Laboratory; 1979.

[53] Hychico. Clean hydrogen production and renewable energy storage. 2017, Presented at Hidrógeno con Energías Renovables, nuevas oportunidades para Chile, Chile 10. May 2017.

[54] Bauer S. Underground sun conversion. 2018, Presented at Cluster Workshop in Berlin 2018.

[55] Hogeweg S, Strobel G, Hagemann B. Simulation of underground microbiological methanation in a conceptional well doublet system. In: DGMK/ÖGEW-Frühjahrstagung. 2019.

[56] Rittmann S, Seifert A, Herwig C. Essential prerequisites for successful bioprocess development of biological ch4 production from co2 and h2. Crit Rev Biotechnol 2015;35(2):141–51. http://dx.doi.org/10.3109/07388551.2013.820685, arXiv:https://doi.org/10.3109/07388551.2013.820685.

[57] Luo G, Angelidaki I. Integrated biogas upgrading and hydrogen utilization in an anaerobic reactor containing enriched hydrogenotrophic methanogenic culture. Biotechnol Bioeng. 109, 11 p.2729–2736, arXiv:https://onlinelibrary.wiley.com/doi/pdf/10.1002/bit.24557, URL https://onlinelibrary.wiley.com/doi/abs/10.1002/bit.24557, http://dx.doi.org/10.1002/bit.24557.

[58] Grimalt Alemany A, Skiadas I, Gavala H. Syngas biomethanation: State-of-the-art review and perspectives. Biofuels, Bioprod Biorefin 2018;12:139–58. http://dx.doi.org/10.1002/bbb.1826.

[59] Kimmel DE, Klasson KT, Clausen EC, Gaddy JL. Performance of trickle-bed bioreactors for converting synthesis gas to methane. Appl Biochem Biotechnol 1991;28(1):457. http://dx.doi.org/10.1007/BF02922625.

[60] Westman SY, Chandolias K, Taherzadeh MJ. Syngas biomethanation in a semi-continuous reverse membrane bioreactor (rmbr). Fermentation 2016;2(2). http://dx.doi.org/10.3390/fermentation2020008, URL http://www.mdpi.com/2311-5637/2/2/8.

[61] Lecker B, Illi L, Lemmer A, Oechsner H. Biological hydrogen methanation – a review. Bioresour Technol 2017;245:1220–8. http://dx.doi.org/10.1016/j.biortech.2017.08.176, URL http://www.sciencedirect.com/science/article/pii/S0960852417314906.

[62] Hagemann B, Ganzer L, Panfilov M. Field scale modeling of bio-reactions during underground hydrogen storage. 2018, http://dx.doi.org/10.3997/2214-4609.201802116.

[63] Zapf M. Stromspeicher und Power-to-Gas im deutschen Energiesystem. 2017, http://dx.doi.org/10.1007/978-3-658-15073-0.

[64] Henning H-M, Palzer A. Energiesystem Deutschland 2050. Fraunhofer-Insitut für Solar Energiesysteme; 2013.

[65] Ullrich T, Linder J, Bär K, Mörs F, Graf F, Lemmer A. Influence of operating pressure on the biological hydrogen methanation in trickle-bed reactors. Bioresour Technol 2017;247:7–13. http://dx.doi.org/10.1016/j.biortech.2017.09.069.

[66] The potential of hydrogen for decarbonization of german industry - a joint study by equinor and oge management summary. Equinor & Open Grid Europe; 2019.

[67] Kraus N. Hydrogen europe vision on the role of hydrogen and gas infrastructure on the road toward a climate neutral economy - A contribution to the transition of the gas market. Hydrogen Europe; 2019.