

## Power to Gas projects review: Lab, pilot and demo plants for storing renewable energy and CO<sub>2</sub>



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### ABSTRACT

Power to Gas (PtG) processes have appeared in the last years as a long-term solution for renewable electricity surplus storage through methane production. These promising techniques will play a significant role in the future energy storage scenario since it addresses two crucial issues: electrical grid stability in scenarios with high share of renewable sources and decarbonisation of high energy density fuels for transportation. There is a large number of pathways for the transformation of energy from renewable sources into gaseous or liquid fuels through the combination with residual carbon dioxide. The high energy density of these synthetic fuels allows a share of the original renewable energy to be stored in the long-term. The first objective of this review is to thoroughly gather and classify all these energy storage techniques to define in a clear manner the framework which includes the Power to Gas technologies. Once the boundaries of these PtG processes have been evidenced, the second objective of the work is to detail worldwide existing projects which deal with this technology. Basic information such as main objectives, location and launching date is presented together with a qualitative description of the plant, technical data, budget and project partners. A timeline has been built for every project to be able of tracking the evolution of research lines of different companies and institutions.

### 1. Introduction

One of the targets related to renewable energy penetration enclosed in the roadmap of the European Commission for 2020 is the achievement of a 20% of renewable energy in the overall energy mix of the European Union. In fact, renewables will continue to play a key role in helping the EU meet its energy needs beyond 2020 since EU countries have already agreed on a new renewable energy target of at least 27% of final energy consumption in the EU as a whole by 2030. Thus, renewable energy sources such as solar or wind will play a significant role in electric power generation. The last progress report towards the EU's 2020 renewable energy goals published in June 2015 presents an average share of the renewable electricity supply of 24% with strong differences among countries [1]. While countries as Malta have reached shares of renewable electricity production near 1%; shares above 60% have already been reached in several European countries such as Sweden and Austria becoming in some cases the largest primary source

of electricity [2].

Given the fluctuating and intermittent nature of these energy sources, mismatches between supply and electrical demand which affect to security and stability of the grid will appear. These mismatches must be balanced for grid stability purposes. This has become a critical challenge for future society which must be tackled by developing innovative energy storage solutions. Current storage systems present low energy density or limited storage potential. Therefore, new technologies must be developed to overcome these limitations and increase reserve production ratio.

A large number of pathways exists for the transformation of renewable energy into gaseous or liquid fuels through the combination with residual carbon dioxide. Up to now, a clear classification of these processes is not presented in literature. Thus, some confusion may appear when referring these new storage systems which convert solar energy or power from renewable into fuels. Among them, Power to Gas processes appear as promising systems which convert electricity into

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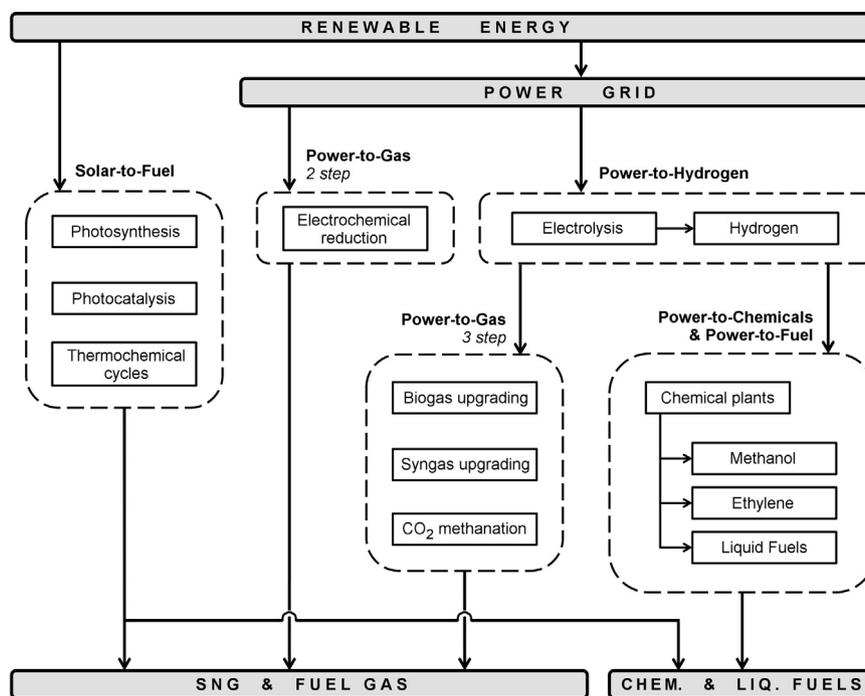


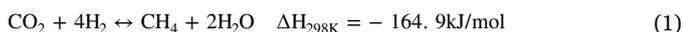
Fig. 1. Renewable energy and CO<sub>2</sub> hybrid storage techniques.

synthetic natural gas. The features of this technology allow the connection of electrical and gas networks in a single energy system introducing high flexibility in the balance of the grid [3].

The first objective of this work is to outline a generalization of the PtG concept, thus giving to the reader a more structured understanding of what is behind these ideas. Since there exists a lack of detailed information in literature referred to this promising long-term electricity storage technique, the second objective of the review is to compile worldwide PtG projects specifications in a structured manner. Thus, we present a thorough review which gathers the construction and operation of pilot-, demo- and lab plants destined to the storage of electricity into SNG.

## 2. Hybrid storage of renewable energy and CO<sub>2</sub>

The Power to Gas concept, storage of renewable energy and carbon dioxide as natural gas, was first proposed by Koji Hashimoto in 1994 [4]. The difficulties associated to large-distance electricity transport in Japan inspired the research on energy carriers. The combination of electrolysis –run by solar energy– and the Sabatier reaction (Eq. (1)) allowed methane synthesis and the subsequent distribution of renewable electricity without the requirement of new infrastructures or alternative combustion systems. Moreover, as CO<sub>2</sub> is recycled, the global warming would be mitigated in some extent [5].



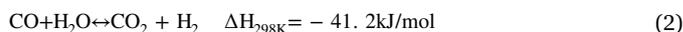
In 2009, Michael Sterner refreshed the Power to Gas concept to focus on the storage of the increasing renewable power surplus, rather than on electricity transportation necessities. Several configurations were outlined depending on the carbon dioxide source used in the methanation stage (biogas, syngas or pure CO<sub>2</sub>) [3]. The simplest integration directly transforms CO<sub>2</sub> from carbon capture techniques, e.g. post-combustion and oxyfuel combustion. Other possibility involves the methanation of biogas produced by anaerobic digestion of biomass or wastes. In this case, methanation may be carried out by directly adding hydrogen, since biogas is mainly composed by CO<sub>2</sub> and CH<sub>4</sub>.

Traditionally, biogas had always been upgraded through the separation of both components to reject CO<sub>2</sub> and obtain a purified

stream of methane [6]. This option cannot be considered as a Power to Gas technique since it neither stores electricity nor makes use of the carbon dioxide obtained in the fermentation process.

Similarly, Sterner proposed the upgrading of gasification syngas through the addition of renewable hydrogen –hydrogen obtained from renewable energy sources– as an alternative Power to Gas concept. Syngas is mainly composed by CO, CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>, with specific volumetric fractions that significantly vary depending on the feedstock and the gasification process involved [7]. The hydrogen content is hardly ever enough to transform the whole amount of CO and CO<sub>2</sub> through a stoichiometric Sabatier process. Hence, the addition of hydrogen would be required to achieve complete methanation of these compounds.

Obtaining synthetic natural gas (SNG) from coal gasification syngas reached a commercial stage of development in the 80/90's [8], while from biomass syngas recently reached the demonstration scale with a 20 MW facility built in the framework of the GoBiGas project [9]. The CO:H<sub>2</sub> ratio of the syngas is commonly adjusted in a subsequent stage by means of water-gas shift reaction (Eq. (2)) without adding renewable H<sub>2</sub>, and later removing the remaining CO<sub>2</sub> [10,11]. As stated for traditional biogas upgrading, this conventional syngas upgrading plants cannot be considered as Power to Gas concepts.



The very first PtG concept was associated with water dissociation by means of electrolyzers to directly generate hydrogen from an electric input. Hence, initial references to Power to Gas concept were only related to the production of H<sub>2</sub> from renewable energy sources (i.e. Power to Hydrogen) [12]. Great efforts have been done worldwide to develop a hydrogen-based economy and it has been proven that its definitive deployment is limited, among others, by the requirement of larger hydrogen infrastructure and a well-established hydrogen market [13]. Thus, several researchers left behind the initial Power to Hydrogen concept and proposed new configurations focused on the generation of other gaseous fuels such as methane to take advantage from the natural gas infrastructure.

The proposed generalization of Power to Gas concept, inspired by the initial ideas of Hashimoto in 1994, involves the simultaneous storage of carbon dioxide and renewable energy surplus in the form of a

**Table 1**  
Summary of selected reviews of renewable energy and CO<sub>2</sub> hybrid storage techniques (2010 onwards).

Review	Path	Focus
Bennamoun, 2015[34]	Photosynthesis	Drying methods for algae
Bharathiraja, 2015[35]	Photosynthesis	Algae cultivation methods and processing technologies
Chen, 2015[36]	Photosynthesis	Microalgae productivity and influencing factors toward biofuel production
Sarsekeyeva, 2015[37]	Photosynthesis	Developments of biofuels produced from cyanobacteria
Song, 2015[38]	Photosynthesis	Feature and applications of brown algae
Sutherland, 2015[39]	Photosynthesis	Limitations and improvements of algae in light absorption and utilization
Trentacoste, 2015[40]	Photosynthesis	Policies for algae cultivation
Vijayakumar, 2015[41]	Photosynthesis	Potential pharmaceutical applications of cyanobacteria
Han, 2014[42]	Photosynthesis	Algae waste composting
Chow, 2013[43]	Photosynthesis	Thermal chemical transformation of algae to biofuels
Razzak, 2013[44]	Photosynthesis	Microalgae culturing for CO <sub>2</sub> capture, waste-water treatment and biofuel production
Menetrez, 2012[45]	Photosynthesis	Environmental impact issues of algae
Rosgaard, 2012[46]	Photosynthesis	Genetic engineering for improving carbon fixation in cyanobacteria
Quadrelli, 2011[14]	Photosynthesis Power to Chemicals	Large-volume routes for chemical utilization of CO <sub>2</sub> at preindustrial level
Brennan, 2010[47]	Photosynthesis	Algae production, harvesting and conversion to fuel
Kunjapur, 2010[48]	Photosynthesis	Large-scale reactors used to cultivate microalgae for biofuel production
Mata, 2010[49]	Photosynthesis	Production and processing of microalgae for biodiesel production
Ola, 2015[27]	Photocatalysis	Reduction by TiO <sub>2</sub> photocatalyst. Material design and reactor configurations
Das, 2014[50]	Photocatalysis	Photocatalysts and reactor systems for CO <sub>2</sub> transformation into fuels
Li, 2014[51]	Photocatalysis	Material design and reactor engineering
Liu, 2014[52]	Photocatalysis	Reduction with H <sub>2</sub> O by TiO <sub>2</sub> photocatalyst
Sun, 2014[53]	Photocatalysis	Reduction by nanostructured carbon catalyst
Habisreutinger, 2013[54]	Photocatalysis	Heterogeneous reduction by metal oxides, oxynitrides, sulphides and phosphides
Izumi, 2013[55]	Photocatalysis	Photocatalysis with water, hydrogen and recycling electron donors
Tahir, 2013[56]	Photocatalysis	Developments and applications of visible light responsive TiO <sub>2</sub> photocatalysts
Ganesh, 2011[57]	Photocatalysis	Reduction to Methanol
Agrafiotis, 2015[30]	Thermochemical cycles	Types of cycles, heat transfer issues and reactors employed
Scheffe, 2014[58]	Thermochemical cycles	Comparison of physical properties between metal oxide materials
Roeb, 2012[59]	Thermochemical cycles	Reactor technologies and

(continued on next page)

**Table 1 (continued)**

Review	Path	Focus
Loutzenhiser, 2010[60]	Thermochemical cycles	material properties regarding its technical implementation Kinetics, reactor technology and economics for Zn/ZnO cycles
Albo, 2015[31]	Electrochemical reduction	Reduction to methanol. Cathode materials, reaction media, cells and working conditions
Jones, 2014[61]	Electrochemical reduction	Comparison between methods
Lim, 2014[62]	Electrochemical reduction	SOFC, metal electrodes in aqueous solution and molecular catalysts
Qiao, 2014[32]	Electrochemical reduction	Catalysts for the reduction to low-carbon fuels
Costentin, 2013[63]	Electrochemical reduction	Comparison of performances between catalysts
Jhong, 2013[64]	Electrochemical reduction	Current status and remaining challenges
Kondratenko, 2013[65]	Electrochemical reduction Photocatalysis	Design of metal electrodes and alternative approaches
Rittman, 2015[66]	Biogas upgrading	Scale-up issues for biological CH <sub>4</sub> production
Götz, 2016[67]	Biogas upgrading Syngas upgrading CO <sub>2</sub> methanation	Technological and economic issues of Power-to-Methane
Rönsch, 2016[68]	Biogas upgrading Syngas upgrading CO <sub>2</sub> methanation	Methanation fundamentals (catalysts, mechanisms and modelling) and reactor concepts
Aziz, 2015[69]	Power-to-Chemicals	Reaction mechanism over heterogeneous catalysts
Gao, 2015[70]	Power-to-Chemicals	Methanation catalysts research and development
Wang, 2011[71]	Power-to-Chemicals	Catalytic reactivity and reaction mechanisms over heterogeneous catalysts
Ganesh, 2014[72]	Power-to-Fuel Solar-to-Fuel	Conversion of CO <sub>2</sub> into methanol using any renewable energy source

valuable product. The classification of those techniques included under this definition is illustrated in Fig. 1.

Chemical products that require hydrogen and carbon dioxide in their production process could also be considered as hybrid energy storage when H<sub>2</sub> is renewably produced from surpluses. Some important chemicals in this field are methanol, ethylene, propylene, formic acid and liquid fuels [14]. They can directly use CO<sub>2</sub>, or convert the CO from a prior reverse water-gas shift reaction (reverse Eq. (2)).

Besides the commercial processes for the production of chemicals that can be converted into hybrid storage concepts, various novel processes under research would extend the term as well. They are grouped into 1-step or 2-step processes, depending on the number of stages required to transform renewable energy into final products [15].

The 1-step paths directly convert sunlight into valuable products, without an intermediate transformation into electricity. It is worthy to distinguish three of these storing processes capable of consuming CO<sub>2</sub>: (i) photosynthesis-based metabolic routes, (ii) photocatalysis and (iii) thermochemical cycles.

Biological capture of CO<sub>2</sub> fixes carbon and sunlight as chemical energy contained in newly grown organisms by means of photosynthesis. Since the efficiency of photosynthesis increases when generated organic structures present very small sizes, single-cell microalgae and cyanobacteria are the common options for this kind of process. Photons are absorbed by antenna proteins thus transferring their energy to the production of storage components, e.g., glucose, carbohydrates, lipids

and proteins [16,17]. The development of biofuels from algal biomass is currently focused on addressing related environmental, technological and economic drawbacks, since the lab-scale phase has been completed successfully [18]. However, algae are already commercially applied in other non-energetic uses as pharmaceuticals [19,20], cosmetics [21,22] and animal feed [23,24]. Contrarily, biofuels from cyanobacteria are still far from its commercial development since greater efficiencies and improved reactor designs are needed [25,26].

In photocatalysis, as in electrochemical processes, carbon dioxide is reduced by means of an electric current. The difference between both techniques is the nature of the electrons that produce the electricity, since photocatalysis is generated by the absorption of a photon in semiconductor materials, thus producing a current based in electron-hole pairs [16]. CO<sub>2</sub> photocatalysis is still not feasible due to the absence of scalable reactors able to produced significant quantities of fuel [27].

Thermochemical cycles reduce metal oxide materials (Eq. (3)) inside cavity receivers in concentrating solar plants at high temperatures (1200–1600 °C). Later, when the metal oxide is regenerated by oxidation with carbon dioxide, it is obtained a syngas mainly composed of CO that can be methanized (Eq. (4)) [28,29]. The technique has already been successfully demonstrated at bench- and pilot-scale, but some crucial technical challenges remain unsolved for its commercial exploitation [30].



The 2-step method involves the electrochemical reduction, where electrical energy is supplied to establish a potential between two electrodes in order to allow CO<sub>2</sub> to be transformed into reduced forms [31]. Hence, renewable energy must be previously converted to electricity and later to the valuable chemical. Some of the most interesting products that could be included in the scheme through this method are formic acid, methanol and methane, which are produced by two-, six- and eight-electron reduction pathways, respectively [32]. However significant improvements in energy efficiency are needed before this technique becomes cost effective, in comparison with the current ways to produce the same products [33].

A large number of reviews has been published so far in reference to the development of these conversion paths studying different aspects (Table 1). However, none of them is focused on 3step-Power to Gas plants and their future perspectives. Therefore, the main objective of the present review is to gather those research projects concerning the construction or management of pilot- and demonstration plants which carry out 3step-Power to Gas paths, thus summarizing the state of the art of the technology.

### 3. Review of Power to Gas (3 step) projects

In this section a thorough review of 3step-Power to Gas projects which investigate methanation through the application of renewable hydrogen (at least in the conception of the system) is presented.

As a preliminary overview of the information presented in the following, Fig. 2 shows the distribution of the number of projects among countries classified by type of methanation process. Germany is the spearhead nation in developing PtG systems, mainly focused on CO<sub>2</sub> catalytic methanation.

A timeline has been built to clearly represent the evolution and concatenation of worldwide PtG projects with years, Fig. 3. Tohoku University and Hitachi Zosen which initiated their research in PtG systems in 1996 appear as pioneers in this field. As shown in Fig. 3, most of the projects were launched from 2009 onwards when the international community massively discovered the great potential of PtG in excess electricity storage.

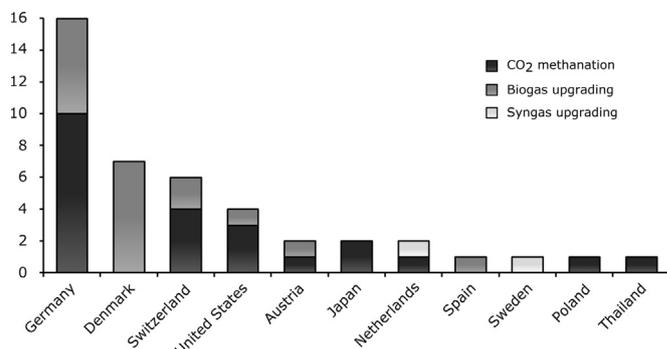


Fig. 2. Existing PtG projects distributed by country and technology.

General information of 3step-Power to Gas projects is summarized in Table 2, where related projects which imply an extension of a previous one are grouped in a same-colour block in order to historically follow the evolution of PtG technology.

There also exist other facilities and projects that apply methanation without making use of renewable hydrogen. However, they are beyond the scope of this review and are not included in the following subsections.

#### 3.1. ETOGAS – Audi e-gas plant

The Audi e-gas plant, under operation since 2013 and located in Werlte (Germany), is the largest industrial Power to SNG facility built in the world (6 MW<sub>e</sub>). It is based in the catalytic methanation of pure hydrogen and carbon dioxide in a single isothermal fixed-bed reactor [73,74].

The hydrogen comes from 3×2.0 MW<sub>e</sub> alkaline electrolyzers powered by an offshore wind park in the North Sea, which comprises 4×3.6 MW<sub>e</sub> turbines and it is co-financed by Audi AG and a regional power-supply company [75]. In addition, the required CO<sub>2</sub> is separated from the raw biogas of a neighbouring biomethane plant, belonging to EWE Biogas GmbH & Co. KG, by means of amine scrubbing [76].

The Power to Gas process of Audi has 54% efficiency (without accounting the utilization of the by-produced thermal energy), thus obtaining a SNG with 13.85 kW h/kg of energy content. The maximum output flow of the facility is 325 Nm<sup>3</sup>/h, but it is only expected a production of roughly 1000 t per year, because of the availability of the renewable energy consumed to produce the hydrogen (4000 h per annum) [77].

The Power to Gas plant, in contrast to the biogas plant, is not operated on a stationary basis but following the energy supply pattern. Furthermore, the plant has been recently qualified for participating in the electricity balancing market, after successfully draw 6 MW<sub>e</sub> of power from the grid within five minutes as well as run prescribed load profiles [78]. The thermal management of the waste heat recovered from electrolysis and methanation, to supply the various heat consumers in the biogas and CO<sub>2</sub> removal plants (mainly amine regeneration), is highly complex [79]. Hence, the assessment and optimization of the plant operation is provided by the WOMBAT simulation [80].

The construction of the plant was born from a collaborative project between Audi AG, ETOGAS GmbH (formerly named Solar Fuel GmbH), the Centre for Solar Power and Hydrogen Research Baden-Württemberg (ZSW), the Fraunhofer Institute for Wind Energy and Energy System Technology (Fraunhofer IWES) and EWE Biogas GmbH & Co. KG [81].

The entire research plan dates back to 2009, in Stuttgart, with ETOGAS as manufacturer and ZSW as the chief developer. The several stages that have been required for achieving the current demonstration plant were performed in Germany in the following order [82]:

- Power to Gas α-plant with air purification (Stuttgart, 2009): A

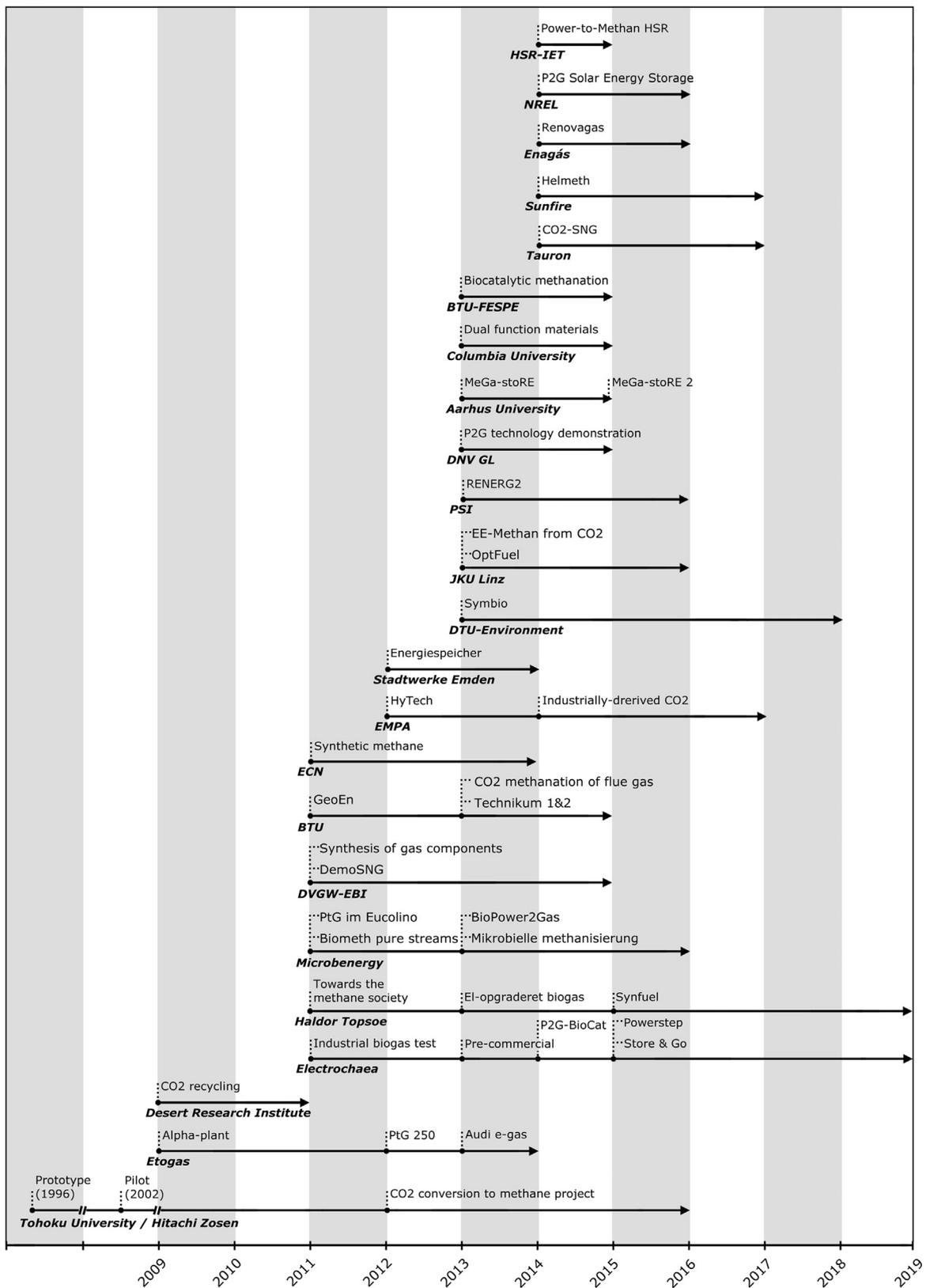


Fig. 3. Timeline of worldwide existing PtG projects.

25 kW<sub>e</sub> electrolyser coupled to a CO<sub>2</sub> ambient air purification system was the initial installation used for demonstrating the basic feasibility of the Power to Gas process. The partner and co-developer of this early research stage was ZSW. The facility was built as a mobile container laboratory with a CH<sub>4</sub>-filling station of 15 kg capacity at

200 bar. The total efficiency achieved without optimizations was 40% [83,84].

- Power to Gas α-plant with CO<sub>2</sub> from biogas purification (Werlte, 2010–2011): The second phase implied the implementation of the methanation with carbon dioxide captured by pressure swing

**Table 2**  
3step-Power to Gas projects.

Process type	Project Name	Location	Period	Institutions	Ref.
CO <sub>2</sub> methanation	Audi e-gas	Werlte, Germany	2013	ETOGAS, ZSW, Fraunhofer IWES, EWE Biogas, Audi	[74,77]
CO <sub>2</sub> methanation	Power to Gas 250	Stuttgart, Germany	2012–2014	ETOGAS, ZSW, Fraunhofer IWES	[84]
Biogas upgrading	Alpha-plant	Bad Hersfeld, Germany	2012	ETOGAS, ZSW, Fraunhofer IWES, HBFZ	[87]
Biogas upgrading	Alpha-plant	Morbach, Germany	2011	ETOGAS, ZSW, Fraunhofer IWES, Juwi	[85,86]
CO <sub>2</sub> methanation	Alpha-plant	Werlte, Germany	2010–2011	ETOGAS, ZSW, EWE Biogas	[85]
CO <sub>2</sub> methanation	Alpha-plant	Stuttgart, Germany	2009	ETOGAS, ZSW	[83]
n/a	STORE & GO	Switzerland, Germany, Italy	2015–2019	Electrochaea, DVGW, E.ON, Regio Energie, EII Spa, HSR, PoliTo, JKU Linz-El, RUG, Atmostat, CEA, Clmeworks, DBI-GUT, BFP, EDI, EMPA, EPFL-IPES, EPFL-MER, EPFL-CEN, Energy Valley	[98,106]
Biogas upgrading	POWERSTEP – Full scale demonstration of energy positive sewage treatment plant concepts towards market penetration	n/a	2015–2018	Electrochaea, KWB, TU Wien, Eawag, Fraunhofer IPM, Veolia, Veolia-WT, NEAS, Biofos, BWB, UBA, APS, Sustec, Atemis, Arctic	[97,104,105]
Biogas upgrading	P2G-BioCat project	Avedøre, Denmark	2014–2016	Electrochaea, Hydrogenics, Audi, NEAS, HMN Gashandel, Biofos, Insero	[90,94,96]
Biogas upgrading	Pre-commercial	Foulum, Denmark	2013	Electrochaea, E.ON, Energie 360°, EWZ, NEAS, AU	[100,102]
Biogas upgrading	Industrial Biogas Test	Chicago, United States	2011	Electrochaea, UChicago, AB InBev	[99,100]
Biogas upgrading	BioPower2Gas	Allendorf, Germany	2013–2016	Microbenergy, Schmack, Carbotech, EnergieNetz, EAM EnergiePlus, CUBE, DBFZ, IdE	[107,108,109]
Biogas upgrading	Mikrobielle Methanisierung	Schwandorf, Germany	2013	Microbenergy, Schmack, FENES, ZVKS	[114,115]
Biogas upgrading	Power-to-Gas im Eucolino	Schwandorf, Germany	2011	Microbenergy, Schmack	[73,112]
CO <sub>2</sub> methanation	Biological methanation of pure streams	Schwandorf, Germany	2011	Microbenergy, Schmack	[73]
CO <sub>2</sub> methanation	HELMETH	n/a	2014–2017	Sunfire, KIT, PoliTo, ERIC, TS-Torino, NTUA, DVGW	[116,123]
Syngas upgrading	SYNFUEL	n/a	2015–2019	Haldor Topsoe, DTU, AAU, Chalmers, DONG, Energinet.dk, INSA, TU Berlin, NU, CAS, MIT, AVL	[137]
Biogas upgrading	El-opgraderet biogas	Foulum, Denmark	2013–2016	Haldor Topsoe, Ea, AU, PlanEnergi, HMN Naturgas, NGF, EnergiMidt, DGC, Cemtec, Xergi	[124,125]
Biogas upgrading	På Vej Mod Metansamfundet /Towards the methane society	Midtjylland, Denmark	2011–2012	Haldor Topsoe, AU, AgroPark, HIRC, Planenergi, GreenHydrogen, HMN Naturgas, Lemvig Biogas, DTU, INBIOM	[130]
Biogas upgrading	MeGa-stoRE 2 – Optimising and Upscaling	n/a	2015–n/a	AU, NGF, DTU, Elplatek, GreenHydrogen	[141,142]
Biogas upgrading	MeGa-stoRE – Methane Gas storage of Renewable Energy	Lemvig, Denmark	2013–2015	AU, Elplatek, GreenHydrogen, Lemvig Biogas, DTU-Mekanik, AU Herning	[139]
Biogas upgrading	SYMBIO	Denmark	2013–2018	DTU-Environment, SDU, UM, Energinet.dk, Maabjerg BioEnergy	[143,145]
Biogas upgrading	RENOVAGAS	Spain	2014–2016	Enagas, ICP-CSIC, CNH2, FCC-Aqualia, Gas Natural Fenosa, Tecnalia, Abengoa	[146,147]
CO <sub>2</sub> methanation	Technical assumptions, technology demonstration and results P2G project	Rozenburg, Netherlands	2013–2015	DNV GL, TKI Gas, Stedin, Rotterdam Council, Ressor Wonen	[148,151]
Syngas upgrading	Synthetic methane: a medium for storage and transportation of excess renewable energy	Netherlands	2011–2014	ECN, TU-Delft, Hanze UAS	[153,156,157]
Syngas upgrading	DemoSNG	Köping, Sweden	2011–2015	DVGW-EBI, KIT, KTH, Cortus, Gas Natural Fenosa	[160,163]
CO <sub>2</sub> methanation	Storage of electric energy from renewable sources in the natural gas grid – water electrolysis and synthesis of gas components	Baden-Wurtemberg, Germany	2011–2014	DVGW-EBI, EnBW, Fraunhofer ISE, H-Tec, IoLiTec, Outotec	[165,167]
CO <sub>2</sub> methanation	CO <sub>2</sub> -SNG	Poland	2014–2017	Tauron, CEA, Atmostat, AGH-UST, IChPW, Rafako, WT & T Polska	[170,173,174]
CO <sub>2</sub> methanation	CO <sub>2</sub> recycling via reaction with hydrogen	Reno, United States	2009	DRI, RCO <sub>2</sub> AS	[175,176]
CO <sub>2</sub> methanation	Pilot- und Demonstrationsanlage Power-to-Methane HSR	Rapperswil, Switzerland	2014–2015	HSR-IET, HSR, Audi, Climeworks, Erdgas Obersee, Erdgas Regio	[177,178]
Biogas upgrading	Kommunale Kläranlagen als Energiespeicher	Emden, Germany	2012–2014	Stadtwerke Emden, BEE, Thalen Consult, ibis Umwelttechnik, GA-Group	[184,185,186]
CO <sub>2</sub> methanation	CO <sub>2</sub> Conversion to Methane Project	Rayong, Thailand	2012–2016	Hitachi Zosen, DAE, PTTEP	[188,190]
CO <sub>2</sub> methanation	Pilot plant – Tohoku Institute of Technology	Tohoku, Japan	2002–2005	Tohoku University, TohTech, Hokudai, DAE, NRIM, MES, Ryoka	[194,195]
CO <sub>2</sub> methanation	Prototype plant – Tohoku University	Tohoku, Japan	1996	Tohoku University, IMR, TohTech, Hokudai, DAE, NRIM, MES, Ryoka	[194,195]
CO <sub>2</sub> methanation	EE-Methan from CO <sub>2</sub>	Leoben, Austria	2013–2016	JKU Linz, MU Leoben, TU Wien, Christof Group, Profactor, ÖVGW, FGW	[198,203,204]
Biogas upgrading	OptFuel	Leoben, Austria	2013–2016	JKU Linz, MU Leoben, TU Wien, Christof Group, Profactor, ÖVGW, FGW	[199,204,207]
CO <sub>2</sub> methanation	P2G Solar Energy Storage RD & D	Golden, United States	2014–2016	NREL, SoCalGas	[209,210]
CO <sub>2</sub> methanation / Biogas upgrading	RENERG <sup>2</sup>	Villigen, Switzerland	2013–2016	PSI, EMPA, ETH Zurich, ZHAW, EPFL	[212,214]
CO <sub>2</sub> methanation	Catalytic methanation of industrially-derived	Dübendorf, Switzerland	2014–2017	EMPA, ZHAW	[218,220]

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Table 2 (continued)

Process type	Project Name	Location	Period	Institutions	Ref.
Biogas upgrading	CO <sub>2</sub> SmartCat	Switzerland Dübendorf, Switzerland	n/a	EMPA, ZHAW, Zeochem, VSG	[217,219]
CO <sub>2</sub> methanation	HyTech	Switzerland Dübendorf, Switzerland	2012–2015	EMPA, ZHAW, EPFL, PSI	[212]
CO <sub>2</sub> methanation	CO <sub>2</sub> -Methanation of flue gas	Brandenburg, Germany	2013–2015	BTU, Panta Rhei, Vattenfall	[222,223,225]
CO <sub>2</sub> methanation	CO <sub>2</sub> catalysis, pilot plant - Technikum 1 & 2	Cottbus, Germany	2013–2014	BTU	[225,230]
CO <sub>2</sub> methanation	GeoEn	Cottbus, Germany	2011–2013	BTU, GFZ, Uni-Postdam	[227,228,229]
CO <sub>2</sub> methanation	Dual function materials for CO <sub>2</sub> capture and conversion using renewable H <sub>2</sub>	New York, United States	2013–2015	Columbia University, BASF	[232,233,234]
CO <sub>2</sub> methanation	Biocatalytic methanation in an anaerobic three-phase system	Cottbus, Germany	2013–2015	BTU-FESPE	[235,236]

\*Note: Photo-electrochemical water splitting.

adsorption (PSA) from the EWE Biogas plant. Hence, the  $\alpha$ -plant was tested at the current location of the Audi e-gas project, and it was formed a three member alliance [85].

- Power to Gas  $\alpha$ -plant with raw biogas (Morbach, 2011): For the first time, the  $\alpha$ -plant was operated with raw biogas instead of pure CO<sub>2</sub>. It was demonstrated that direct methanation of biogas is technically feasible in a PtG plant. In this stage, Juwi AG joined to the previous partners [85,86].
- Power to Gas  $\alpha$ -plant in long period operation with raw biogas (Bad Hersfeld, 2012): This research stage corresponds to a project launched at the Fraunhofer IWES, in collaboration with ZSW. The target was in situ methanation with raw biogas from an agricultural biogas plant located in the Hessian Biogas Research Centre (HBFZ). The  $\alpha$ -plant property of ETOGAS was integrated in the already existent infrastructure for long period operation despite the fluctuating raw biogas composition [87].
- Power to Gas 250 kW<sub>e</sub> test facility (Stuttgart, 2012–2014): ZSW, Fraunhofer IWES and ETOGAS developed the largest PtG plant of this type at that time [88]. The main objective was to examine and test different fixed-bed reactor technologies for methanation (plate versus tubular reactor construction) [74]. The system is composed by two fixed-bed reactors, with a capacity for 50 l of catalyst. The first one is refrigerated by water, whilst the other by molten salt. Also, there exists a condensation stage between both methanators, and a recirculation of the final gas towards the first reactor [84]. The methane content achieved is 99%, thanks to processing the gas with membrane technology after methanation. Furthermore, the 250 kW alkaline pressure electrolyser was operated in dynamic and intermittent mode, enabling flexible respond to fluctuating solar and wind energy supplies [82].

Its main goal was to reach commercialized PtG systems around 20 MW between 2015 and 2017, with efficiency above 80% thanks to the recovery of the extra thermal heat from methanation [89].

### 3.2. *Electrochaea – BioCat*

The Power-to-Gas via Biological Catalysis (P2G-BioCat) project, which was launched in February 2014 [90], aims to develop the world's largest commercial-scale plant for converting biogas into methane through biological methanation [91]. The facility, located in Avedøre (Denmark), will be operated in dynamic mode to demonstrate its ability to provide energy storage services to the Danish energy system [92].

The construction phase began in July 2015 at the Avedøre Wastewater Treatment Plant, and the facility is expected to be operational by April 2016 [93]. The carbon dioxide source may be raw biogas from an anaerobic digester (60% CH<sub>4</sub> and 40% CO<sub>2</sub>) or pure CO<sub>2</sub> supplied by a conventional biogas upgrading system [94]. The

hydrogen will come from a 1 MW<sub>e</sub> alkaline electrolyser provided by Hydrogenics, which is scheduled to be shipped in early December 2015 [95]. It will be fed with local excess wind power, and the by-product oxygen will be recycled into the wastewater treatment process. Additionally, the heat from methanation will be also integrated, and the final synthetic natural gas produced is destined to be injected into the 4 bar distribution grid [96].

The methanation will be performed in a liquid phase reactor by methanogenic archaea, a single-celled microorganism which has been selectively evolved through survival tests by Electrochaea GmbH. It metabolizes the hydrogen and carbon dioxide to methane in sequential reduction steps in which the 98.6% of carbon is fixed into the product. The archaea works at low temperatures (60–65 °C) and present high tolerance for hydrogen sulfide, nitrogen oxides, ammonia, particles, as well as partial tolerance for oxygen and ethanol [96].

The project has an overall budget of €6.7 million partially supported by the ForskEL-programme (€3.7 million), which is managed by Energinet.dk, the operator of the Danish power and gas transmission grids. The beneficiary consortium is led by the developer of the methanation technology, Electrochaea, and includes the partners Hydrogenics, Audi, NEAS Energy, HMN Gashandel A/S, Biofos A/S, and Insero Business Services [91,92].

The previous research necessary to achieve the current state of development in this project has passed through three relevant phases. Furthermore, Electrochaea participates in two new H2020 projects that has been recently launched following BioCat [97,98]. The three previous research stages and the newly started H2020 projects are summarized in the following:

- Basic research and proof of concept (2006–2010): The scientific basis of the technology was established in The University of Chicago by Dr. Laurens Mets, the inventor of Electrochaea's biocatalyst [86,96].
- Lab-scale 1 kW (2011): Electrochaea successfully tested the biocatalytic capability of archaea using raw biogas coming from the digester of a brewery waste plant located in St. Louis. It contained 30% CO<sub>2</sub>, 68% CH<sub>4</sub> and up to 7000 ppm of hydrogen sulfide [99,100].
- Pre-commercial 250 kW (2013): Electrochaea demonstrated the technology in a pre-commercial setting using a 10,000 l non-optimized reactor, a 250 kW PEM electrolyser, and raw biogas [100,101]. The project was operated over 3000 h under realistic market conditions at Aarhus University's Biogas Research Centre in Foulum. It was partially funded with a grant of €0.88 million from the Danish Energy Agency [102], and the partners of the project were E.ON AG, Energie 360° AG, Elektrizitätswerk der Stadt Zürich (EWZ), and NEAS Energy [103].
- POWERSTEP (2015–2018): This project, launched in September 2015, aims to convert wastewater treatment plants in new renew-

able power producers. The concept will be demonstrated in 6 full-scale studies among Austria, Denmark, Germany, Sweden and Switzerland. Different technologies will be implemented, including Power to Gas developed by Electrochaea. The budget amounts to €5.2 million, and is funded with €4.0 million through the H2020 programme [104,105].

- STORE & GO (2015–2019): Up to 19 industrial and academic partners will demonstrate Power to Gas technology in Switzerland, Germany and Italy, for preventing further construction of new power lines. The project began in September 2015 and puts together multiple institutions researching on methanation like the Swiss Federal Institute of Technology in Lausanne (EPFL), the Swiss Federal Laboratories for Materials Science and Technology (EMPA) and Deutscher Verein des Gas- und Wasserfaches e.V. (DVGW) [98,106].

### 3.3. MicroEnergy – BioPower2Gas

BioPower2Gas is the first Power to Gas plant based in biological methanation that has achieved the commercial status in the world. This has been constructed in a 3 year project located in Allendorf (Germany) that was launched in September 2013. The first injection of SNG into the national gas grid took place in March 2015, and the finishing certification of the plant was obtained in April 2015 [107].

The equipment of the facility has been provided by subsidiaries of the Viessmann Group. The PtG plant is composed by 2×150 kW<sub>e</sub> PEM electrolyzers and a H<sub>2</sub> buffer from Carbotech, a 5 m<sup>3</sup> biological reactor from MicroEnergy GmbH, and system controls from Schmack Biogas GmbH [107]. Moreover, the biogas can come from the two biogas plants (dry or wet fermentation) that Viessmann owns in the area [108].

The first injection of SNG, into the gas grid, consumed 15 Nm<sup>3</sup>/h of hydrogen for the methanation process. However, the potential production of the electrolyser is 60 Nm<sup>3</sup>/h. Furthermore, Viessmann aims to extend the research up to 1,2 MW<sub>e</sub> aiming to reduce the specific cost of the entire facility from 10,000 €/kW to 1200 €/kW for the year 2017 [109]. In addition to the Viessmann companies, the beneficiary partners are EnergieNetz Mitte GmbH (network operator), EAM EnergiePlus GmbH (utilities company), CUBE (engineering consultants) and the project coordinator Institute decentralised Energy Technologies (IdE). Moreover, the German Biomass Research Centre (DBFZ) has provided scientific support [110].

Prior the BioPower2Gas project, MicroEnergy led the line of research of Viessmann, which could be resumed in four development stages:

- Lab-scale research: The proof of the concept was performed at laboratory with a 10 l reactor, increasing the methane content of biogas from 60% to 95% [111].
- Biological methanation of pure streams: A biological reactor for the methanation of pure carbon dioxide and hydrogen was installed in Schwandorf (Germany), coupled to a 55 kW electrolyser. The reactor worked at ambient pressure and had an external heat supply to achieve the necessary operation temperatures (40–65 °C). The results showed that the reactor was able to handle a flow 30 times its size [73].
- Methanation of raw biogas (2011): The objective of the project was to upgrade biogas, during its formation inside the digester, through biological methanation. The biogas reactor was supplied with maize and grass, whilst the hydrogen came from a 120 kW<sub>e</sub> electrolyser that produced 21.3 Nm<sup>3</sup>/h. The methanogenic bacteria consumed the hydrogen, which was introduced from the bottom, as it rose in the reactor through the viscous liquid. Thus, the methane content increased from 50% to 75% and it was obtained a SNG flow of 5.3 Nm<sup>3</sup>/h [73,112].
- Methanation of biogas from wastewater (2013): MicroEnergy

installed a 180 kW<sub>e</sub> PEM electrolyser at the wastewater plant of Schwandorf (ZVKSW), in collaboration with the Research Centre for Power Grids and Energy Storage (FENES) from Universität Regensburg [113]. The goal was to study the stability and reaction rate of the biological methanation under real conditions, by introducing the hydrogen (approximately 30 Nm<sup>3</sup>/h) directly in the digester as in the previous research [114]. The project budget of €1,42 million was partially funded with a €0.53 million grant [115].

### 3.4. Sunfire – HELMETH

Sunfire GmbH is involved in the HELMETH project (Integrated High-Temperature Electrolysis and Methanation for Effective Power to Gas Conversion), launched in April 2014 with a time horizon of three years. It aims to demonstrate efficiencies above 85% in Power to Gas systems by integrating high temperature electrolysis and CO<sub>2</sub> methanation [116]. Thus, Sunfire continues the research on SOEC technology developed in a prior Power to Liquid project [117,118].

Electrolysis research will be conducted in a 15 kW SOEC [119] working at 800 °C and 15 bar, whilst methanation process will comprise two reactors in series at 300 °C and 30 bar, with intermediate water removal [120] thus producing up to 5.4 m<sup>3</sup>/h (60 kW). The plant is expected to be constructed by mid-2016 [121], managing partial loads down to 20% [120]. Moreover, first results concerning catalyst show higher conversions and stability by adding composite oxides to the γ-Al<sub>2</sub>O<sub>3</sub> substrate [122].

The project consortium is led by the Karlsruhe Institute of Technology (KIT), and formed by Sunfire, Politecnico di Torino (PoliTo), European Research Institute of Catalysis AISBL (ERIC), Turbo Service Torino spa, National Technical University of Athens (NTUA), and DVGW [116]. The budget totals €3.8 million, funded with €2.5 million from the European Union's Seventh Framework Programme [123].

### 3.5. Haldor Topsoe – El-Opgraderet Biogas

The El-Opgraderet Biogas project aims to construct and operate a pilot plant in Foulum (Denmark) that upgrades biogas by consuming hydrogen from a 40 kW<sub>e</sub> SOEC electrolyser. The project was launched in June 2013 for three years [124], but no information has been released so far.

The €5.3 million budget was funded with €3.5 million through the EUDP Danish programme. Moreover, although Haldor Topsoe A/S leads the project, the Aarhus University (AU) received the 70% of the grant for constructing the demonstration plant [125]. The rest of the partners are HMN Naturgas I/S, Naturgas Fyn I/S, EnergiMidt, Xergi A/S, Danish Gas Technology Centre (DGC), PlanEnergi.dk, Ea Energyanalyse A/S, and Cemtec [126].

During the past years, Haldor Topsoe has intensively researched in SOEC electrolysis for PtG, although in a theoretical perspective in most cases. Moreover, another project was launched in July 2015 for the period 2015–2019. Their timeline of research can be summarized as follows:

- GreenSynFuels (2010–2011): This project analysed technologies for the development of methanol and DME as green synthetic fuels, through techno-economical calculations. The most favored concept was the methanol synthesis based on gasification of wood assisted by hydrogen from a SOEC electrolyser [127]. The budget amounted to 190 k€ and was partially funded by the EUDP Danish programme [128].
- Biogas SOEC (2011–2012): The project studied two upgrading routes based in SOEC electrolyzers: the direct methanation of biogas by adding hydrogen, and the co-electrolysis of biogas with steam to produce CO and H<sub>2</sub> for a subsequent methanation. Furthermore, the presence of sulphur in the biogas supplied to the SOEC was

investigated experimentally [129]. The budget of the project was 180 k€ (67% funded by the ForskNG programme) [128].

- Towards the Methane Society (2011–2012): Haldor Topsoe constructed a three-reactor pilot plant for purifying biogas, which was operated for 1000 h at the Aarhus University. The two first reactors reduced the sulphur content below 0.04 ppmv, and the third removed the remaining traces. Moreover, the hydrogen was supplied prior the entrance of the last cleaning reactor to consume the oxygen contained in the biogas, thus preparing it for the Sabatier reaction. However, no methanation experiments were performed. Furthermore, the El-opgraderet biogas project, which is currently in progress, arose from this research as a second development phase [130]. The budget amounted to 214 k€ [131].
- CO<sub>2</sub> Electrofuels (2011–2013): This project quantified the cost potential of several fuel synthesis (methane, methanol and DME), and elaborated a roadmap for their introduction in the Nordic region [132]. The research was funded by the Nordic Energy Research Programme [133].
- Green Natural Gas (2011–2014): The Green Natural Gas project identified CO<sub>2</sub> and heat sources for methanation based on SOEC, and provided a technology roadmap through cost-analysis [134,135]. Moreover, dynamic properties for SOEC were tested at Haldor Topsoe facilities. The budget amounted to €3.2 million and was funded with €1.7 million through the EUDP programme [136].

Besides biogas upgrading, Haldor Topsoe has launched a new project named SYNFUEL (2015 – 2019) to explore a PtG process in which carbon source comes from syngas. This project aims to be a proof-of-principle of the combination of SOEC electrolysis and oxygen-blow gasification of biomass. Innovation Fund Denmark granted the project with €2.8 million, whose budget amounts to €3.8 million [137].

### 3.6. Aarhus University – MeGa-stoRE

The MeGa-stoRE (Methane Gas Storage of Renewable Energy) project has developed a proof-of-concept plant for upgrading biogas through catalytic methanation. Aarhus University launched the project in 2013 for two years, inspired by its participation in the Towards the Methane Society project [138]. It was initially located in its Department of Business Development and Technology (AU Herning) for designing and construction, later continued at GreenHydrogen.dk for testing, and finally the equipment was mounted in a container and transported to Lemvig Biogas Amba for operation [139].

The plant comprises a cleaning unit and a methanation reactor. Firstly, a two-step catalytic process purifies biogas and converts contaminants into micronutrients for the digested slurry. Thus, the H<sub>2</sub>S content is maintained below 30 ppb. After cleaning, biogas is methanated using bottled hydrogen, in a single air-cooled reactor [139].

The technology was verified in four long-term tests ranging from 15 to 24 h. All the experiments showed stability and final methane contents between 97–99%. The reactor temperature was set to 270 °C, the pressure was kept at 8 bars and the biogas flow rate was 720 L/h [139].

Besides Aarhus University, which was the project manager, five more partners conformed the consortium: GreenHydrogen, Elplatek A/S, Lemvig Biogas, Department of Mechanical Engineering of the Technical University of Denmark (DTU-Mekanik), and AU Herning [139]. The ForskEL programme partially funded the budget of 900 k€ with a 300 k€ grant [140]. Furthermore, DTU-Mekanik has continued the research by launching a pre-commercialisation project called MeGa-stoRE Optimising and Upscaling, for 2015 onward. The budget amounts to €3.5 million, and ForskEL grants the 25% [141]. The new objective is to achieve SNG productions of 10 Nm<sup>3</sup>/h [142].

### 3.7. Technical University of Denmark - SYMBIO

Besides the collaborative projects with Aarhus University and Haldor Topsoe, the Technical University of Denmark (DTU) leads the SYMBIO project. This research aims to develop the biogas upgrading through the injection of renewable hydrogen into the anaerobic digester. The project was launched in 2013 with a time horizon of five years [143], although DTU had developed previous research experiences in this topic [144].

The two main objectives of the project are to establish a technical solution for the hydrogen injection, and to evaluate the increment in the biogas produced by a secondary injection of CO<sub>2</sub>. However, no results have been released so far [145].

The project consortium is composed by the Department of Environmental Engineering of the Technical University of Denmark (DTU-Environment), University of Southern Denmark (SDU), Energinet.dk, Maabjerg BioEnergy A/S, and the Department of Microbiology and Immunology from the University of Montreal (UM-DMI). The budget amounts to €2.3 million funded with €1.7 million [143].

### 3.8. Enagas – RENOVAGAS

RENOVAGAS aims to develop the first Spanish pilot plant for upgrading biogas through methanation. The project was launched in July 2014, and is planned its conclusion by December 2016. Moreover, as final goal, the SNG produced should have enough quality for its injection to the gas grid [146].

The plant will be constructed along 2015 and operated in 2016. A containerized design will be used for delivering the facility to a biogas plant belonging to FCC-Aqualia S.A., which is expected to produce up to 2 Nm<sup>3</sup>/h of SNG. The pilot will comprise a 15 kW alkaline electrolyser, a modular multichannel reactor with oil-based cooling, and the control systems. The methanator will operate at 25 bar and 275–330 °C with a gas space velocity between 2000 and 20,000 h<sup>-1</sup>, and the catalysts will be made of Ni or Ru, supported on Al<sub>2</sub>O<sub>3</sub> [146].

Enagas S.A., which is the technical manager of the Spanish gas system, leads this project with a consortium composed by the Institute of Catalysis and Petrochemistry (ICP-CSIC), the National Centre for Hydrogen and Fuel Cell Technology (CNH2), FCC-Aqualia, Gas Natural Fenosa, Tecnalia, and Abengoa Hidrógeno. The budget amounts to €1.7 million, and is funded with €1.2 million by the Spanish Ministry of Economy and Competitiveness (MINECO) [146].

Based on the results of this project, it is planned to scale up the system by constructing a 250 kW pilot plant in a second project. Finally, a last stage would build a 5 MW commercial infrastructure [147].

### 3.9. DNV GL – Power to Gas in Rozenburg

The DNV GL Group has developed the first Power to Gas facility in Netherlands. The project objective was to validate the capability of the PtG technology to regulate power production, by injecting SNG into the gas network. The plant, located in Rozenburg, provides natural gas to 30 nearby apartments [148] since its inauguration in October 2014 [149]. The lab-scale research began in 2011 [150], the project was initiated in 2013 and the final report has been released in 2015 [151].

The facility comprises a 7 kW commercial PEM electrolyser (model Hogen S40), a four-reactor methanation system, and two CO<sub>2</sub> tanks, placed in three individual containers. Four solar panels, on the containers' roofs, partially supply the hydrogen production, whilst the electricity grid provides the remaining demand. Moreover, the carbon dioxide comes from a wholesale distributor [151].

The methanators are made of stainless steel 316 L with a capacity of 1.06 L for each, filled with different commercial catalysts depending on H<sub>2</sub> and CO<sub>2</sub> concentrations. The two first reactors use 11%w Ni

catalysts to avoid exceeding the temperature requirements, whilst the third and fourth reactors use 37%w and 54%w Ni contents, respectively. Hence, reactors can work at temperatures between 150–700 °C and pressures below 15 bar, although the best results are obtained at 377 °C and less than 8 bar. Lastly, the entire plant can be started up in approximately 40 min while the electrolyser is completely operative after just 4 min [151,152].

The project emerged from the cooperation between DNV GL, the Rotterdam Council, and Ressorit Wonen, with funding from Stedin (grid operator) and TKI Gas.

### 3.10. ECN – Synthetic Methane

The Synthetic Methane project analysed the upgrading of syngas, by simulation, under scenarios of energy excess –addition of renewable hydrogen– and energy demand –conventional operation by removing CO<sub>2</sub> excess–. Moreover, a novel sorption enhanced methanation was proposed and tested experimentally [153]. The project was launched in November 2011 [154], and later extended to December 2014 through a complementary work-package regarding SOFC [155].

For the thermodynamic simulation, three methanation configurations were considered: 3-reactor and 2-reactor schemes with recirculation over the first methanator, and 3-reactor scheme with recirculation from the second to the first methanator. Results showed that 3-reactor schemes are preferred. Furthermore, recycling over the first methanator reduces the size required for the following reactors and improves the operational control, although the heat available for external integration diminishes. Additionally, it was found that adding renewable H<sub>2</sub> to the syngas upgrading impacts on the economics rather than on methanation efficiency [156].

The experimental tests were performed at the methanation facility of the Energy Research Centre of the Netherlands (ECN), developed during the prior project Advance Green Gas Technology Development, which was focused on the conventional syngas upgrading (i.e., without renewable H<sub>2</sub> addition). This equipment works at 6 bar with a gas space velocity of 2000 h<sup>-1</sup>, and comprises one pre-reformer at 340 °C for the conversion of aromatic hydrocarbons, followed by two methanation reactors at 230 °C and 240 °C, respectively [157].

In the proposed sorption enhanced methanation, zeolite 4A is added to the catalyst to simultaneously dehydrate the SNG inside the reactor. Later, water is desorbed through a regenerative process using heat from methanation. Large methane yields were found even at pressures below 10 bar, thus reducing compression consumptions and increasing efficiency [158].

The project was carried out by ECN, Delft University of Technology (TU-Delft), and Hanze University of Applied Sciences (Hanze UAS). The budget amounted to €1.3 million, and it was financed through the EDGaR programme [154].

### 3.11. DVGW-EBI and KIT – Demo-SNG

The DemoSNG project demonstrated the feasibility of syngas upgrading by developing a new reactor concept based in honeycomb nickel catalyst [159]. The project was launched in 2011 and concluded during 2015 [160].

The pilot plant was installed into a standard container for shipping purposes. Gas Natural Fenosa was in charge of the hydrogen production [161] through PEM electrolysis [162], and KTH Royal Institute of Technology (KTH) of the hot syngas cleaning process (sulphur, nitrogen and ash removal) [160]. Karlsruhe Institute of Technology (KIT) performed the initial tests, and Cortus operated the pilot at their biomass gasification plant in Köping, Sweden [159].

The proposed methanation uses a single reactor that prevents catalyst degradation through an improved temperature control. The heat transfer from the catalyst to the cooling fluid was simplified by immobilising the catalyst on a metallic monolithic structure (honey-

comb). Thus, the process runs below 300 °C [163], and the facility can process up to 14 Nm<sup>3</sup>/h of raw biogas [160].

KIT coordinated the project. Moreover, DVGW-Forschungsstelle at the Engler-Bunte Institute (DVGW-EBI) participated in the research. KTH, Cortus, and Gas Natural Fenosa completed the consortium. The project was supported by KIC InnoEnergy with €4.5 million [159,161].

Furthermore, DVGW-EBI led a related project between 2011 and 2014 [164], called SEE project (Storage of electric energy from renewable sources in the natural gas grid–water electrolysis and synthesis of gas components). Their research focused on comparing fixed-bed and slurry methanators at lab-scale, besides studying dynamic operation of electrolysers [165].

The Fraunhofer Institute for Solar Energy Systems (Fraunhofer ISE) characterized a 6 kW PEM electrolyser, provided by H-Tec Systems, by simulating realistic load profiles [166]. Outotec studied different catalysts in a single fixed-bed reactor by varying the inlet and reaction temperatures as well as the gas space velocity. The methanator was 73 cm high and 10 cm in diameter, with a 10 cm catalyst layer in the middle. It was fed by selecting the gas composition through different pure gas bottles, achieving up to 70% CO<sub>2</sub> conversions [167]. DVGW-EBI developed slurry reactors filled with liquid property of Ionic Liquids Technologies GmbH (IoLiTec) in which catalyst is finely distributed. This fluid efficiently dissipates the reaction heat, thus enabling an accurate temperature control under fluctuating feed streams. Catalyst particles are suspended by the rising gas bubbles and can be replaced during operation. Finally, Energie Baden-Württemberg AG (EnBW) evaluated the economic viability.

Although the SEE project is already concluded, DVGW-EBI is still improving the slurry methanation process by testing two reactors with diameters of 24.6 mm and 54.5 mm, and height/diameter ratios of 26 and 13, respectively [168]. Furthermore, DVGW-EBI and the KIT are also studying together the combination of the slurry reactor in series with the honeycomb methanation [169].

### 3.12. Tauron – CO<sub>2</sub>-SNG

The CO<sub>2</sub>-SNG project (CO<sub>2</sub> methanation system for electricity storage through SNG production) aims to develop a pilot plant for consuming CO<sub>2</sub> from industry facilities [170]. Tauron Group, as leader, launched the project in 2014 [171] and planned the commissioning of the plant for the first quarter of 2017 [172].

The Power to Gas facility will be located in a coal-burning power plant of Tauron, in Poland [172]. The French partners, the Atomic Energy and Alternative Energies Commission (CEA) and Atmosat, have already developed a structured reactor that processes 1 Nm<sup>3</sup>/h with a 95% conversion rate. The final design will treat up to 25 Nm<sup>3</sup>/h and is expected to be delivered in mid-2016 [173]. The AGH University of Science and Technology (AGH-UST) select and test the catalyst for the methanation reaction. The Institute for Chemical Processing of Coal (IChPW) is responsible for capturing the CO<sub>2</sub> from flue gas. A portable amine plant developed in cooperation with Tauron through a previous project [172,174] will be used. West Technology & Trading Polska Sp. will integrate the methanation reactor and auxiliary equipment [172], whilst Rafako S.A. will evaluate a potential commercialisation. The project has been funded through KIC InnoEnergy [170].

### 3.13. Desert Research Institute – CO<sub>2</sub> recycling via reaction with hydrogen

In 2009, the Desert Research Institute (DRI), with financial support from RCO<sub>2</sub> AS, built a lab-scale reactor to demonstrate the feasibility of catalytic methanation. The system was installed in a portable trailer in Reno, United States [175].

A cylindrical vessel, made of 304 L stainless steel, acted as reactor; it was 16.5 cm long, with an outer diameter of 88.9 mm and a wall thickness of 4.6 mm. The catalyst packed bed (PK-7R Haldor Topsoe)

occupied 0.55 L, i.e. a length of 10.9 cm. The gas flowed from top to bottom, and two thermocouples monitored the catalyst temperature [175]. A 5 kW PEM electrolyser, supplied by solar panels and wind turbines [176], produced high purity hydrogen (99.999%), at 13.8 bar, that was stored in four tanks with a total capacity of 0.1 kg. Lastly, the carbon dioxide source was a gas mixture of 2% CO<sub>2</sub> in N<sub>2</sub>, thus allowing various experimental conditions without excessive temperature rises. In fact, two 400-W band heaters had to be installed in the reactor to achieve the operating temperatures [175].

The optimal operating conditions were studied by varying the H<sub>2</sub>:CO<sub>2</sub> ratio, the catalyst temperature and the space velocity. They found a maximum 60% conversion of CO<sub>2</sub> in the range 300–350 °C, using a H<sub>2</sub>:CO<sub>2</sub> ratio of 4, and a 10,000 h<sup>-1</sup> space velocity [175].

### 3.14. HSR-IET – Power-to-Methane HSR

The Institute for Energy Technology of the Hochschule für Technik Rapperswil (HSR-IET) has built and put in operation the first Swiss Power to Gas facility, located in Rapperswil. The Pilot- und Demonstrationsanlage Power-to-Methane HSR project focuses on developing simulation models and plant designs through experimentation for assessing the future role of Power to Gas in the Swiss energy supply [177]. The project started in November 2014, the plant opened in February 2015, and the final report should have been release in December 2015 [178].

The developed plant is an upgrade of the 25 kW prototype that ZSW operated in 2009 in collaboration with their spin-off ETOGAS [178]. The hydrogen is produced with renewable energy provided by the local power company Elektrizitätswerk Jona-Rapperswil AG (EWJR) [179], until a 50 m<sup>2</sup> photovoltaic panel is installed. Moreover, the CO<sub>2</sub> is captured from air, producing up to 4 kg/day [180]. In addition, for first time a Power to Gas plant will integrate the methanation heat in an ambient-CO<sub>2</sub> absorption process [178].

The facility has a maximum output of 1 Nm<sup>3</sup>/h of methane, which is finally compressed for a filling station (20 h are needed to fill up a car tank) [178]. After 500 h of operation, results show an efficiency of 35% without accounting the CO<sub>2</sub> capture consumption –chemical energy contained in the compressed SNG per unit of electrical energy consumed in the facility [181].

Besides the HSR-IET, the consortium is formed by Audi, Climeworks, Erdgas Obersee, Erdgas Regio, and EWJR [178].

Thanks to the development of a pilot plant, the HSR-IET also participates in other two projects by providing experimental data and operating experience: Renewable Methane for Transport and Mobility (RMTM), and SCCER Storage project. The RMTM project focuses on the application of PtG technology through techno-economic assessment of its entire value chain [182]. It started in October 2015, with a time scope of three years and budgeted for €1.0 million. The Paul Scherrer Institute (PSI) is performing a life cycle analysis of the HSR-IET's PtG facility to quantify the environmental impact [183].

### 3.15. HS Emden/Leer-EUTECH – Power to Gas in Emden

The Emden Institute of Environmental Engineering of the Hochschule Emden/Leer (HS Emden/Leer-EUTECH) evaluated the suitability of a wastewater treatment plant as CO<sub>2</sub> supplier for Power to Gas. The project was launched in 2012 and developed during two years [184], including experimental research at lab-scale [185].

A facility was dimensioned during the project, comprising a 312 kW electrolyser and an isothermal reactor at 335 °C with a SNG production of 59 m<sup>3</sup>/h [185]. As a result, it was announced the construction of a pilot plant in the wastewater treatment plant of Emden [186], although no information about it progress has been released so far.

HS Emden/Leer-EUTECH led the project formed by the partners Stadtwerke Emden GmbH, Bau- und Entsorgungsbetrieb Emden (BEE), Thalen Consult, ibis Umwelttechnik GmbH, and Gesellschaft

für Abwasserberatung und Management mbH (GA-Group) [184]. The budget amounted to 185 k€ and was funded with 125 k€ by the Ministerium für Wissenschaft und Kultur (MWK) through the European Regional Development Fund (ERDF) [187].

### 3.16. Hitachi Zosen – CO<sub>2</sub> Conversion to Methane Project

CO<sub>2</sub> Conversion to Methane Project, launched in 2012, aims to develop industrial PtG and construct the first facility in Thailand [188]. They proposed, as main application, to convert CO<sub>2</sub> generated during extraction of natural gas from natural reservoirs [189].

The first phase of the project has been performed using tubular reactors of 5 m long, with a H<sub>2</sub> conversion of 99.3% operating at 200 °C [190]. The process employs ceramic catalyst based on zirconia-samarium, with nickel as active material, which was developed by Hashimoto et al. through previous research [191]. Thus, results have allowed the simulation and design of the plant that will be built in Thailand, with a methane production of 1000 Nm<sup>3</sup>/h [188,192], between 2014 and 2016 [190]. Moreover, hydrogen will be produced by alkaline electrolysers [193] fed with desalinated seawater [191,192].

The partners cooperating in this research are Hitachi Zosen Corporation, Daiki Ataka Engineering Co. –a subsidiary of Hitachi– and PTT Exploration and Production Public Company Limited (PTTEP) –a Thai petroleum corporation– [191]. However, this project could not be possible without the research carried out by Hashimoto et al. in two prior projects since their technology is employed [194]:

- Prototype plant (1996): The Tohoku University developed the first worldwide Power to Gas prototype, located in the roof of its Institute for Materials Research (IMR). The facility comprises two reactor in series with an intermediate water removal [5], an electrolyser fed by a photovoltaic cell, and a CH<sub>4</sub> combustor from which CO<sub>2</sub> is recycled [194].
- Pilot plant (2002–2005): The prototype research was continued by the installation, in 2003, of an industrial pilot plant in the Tohoku Institute of Technology (TohTech). It produced up to 4 Nm<sup>3</sup>/h of H<sub>2</sub> and 1 Nm<sup>3</sup>/h of CH<sub>4</sub> [194]. This second project was funded through a 3-year grant for developing revolutionary technologies within the Millennium Projects framework [195].

### 3.17. JKU Linz-EI - EE-Methan aus CO<sub>2</sub> and OptFuel

The Energy Institute of the Johannes Kepler University Linz (JKU Linz-EI) participates in four connected projects for developing an entire Power to Gas system in Austria [196]. Wind2Hydrogen (2014–2016) built a 100 kW pilot plant with 12 PEM electrolysers [197], EE-Methan aus CO<sub>2</sub> (2013–2016) develops catalytic methanation [198], OptFuel (2013–2016) focuses in biological methanation [199], and Underground Sun Storage (2013–2016) studies the storage of the generated gas [200,201].

The main goal of EE-Methan aus CO<sub>2</sub> project is to develop a ceramic honeycomb catalyst adapted to industrial CO<sub>2</sub> sources for increasing lifetime a 10% with respect to commercial catalysts [202]. For testing, a methanation pilot plant was built in the University of Leoben consisting of three reactors in series with intermediate cooling. The operating window allows inlet temperatures up to 350 °C and pressures between 1 and 20 bar, with a maximum flow of 3 Nm<sup>3</sup>/h [203,204]. Secondary objectives imply conditioning product gases by using membrane technology, environmental assessment and economic evaluation [205].

The second methanation project, OptFuel, focuses on hydrogen production through fermentation and on the purification requirements for its later conversion into methane. Minor goals as cost assessment and life-cycle analysis are also included [206]. The experimental methanation research is also performed at the pilot plant of MU Leoben, thus studying the potential of combining biological and

chemical processes [204,207].

The consortium of the methanation projects is completed by the Vienna University of Technology (TU Wien), the Austrian Association for Gas and Water (ÖVGW), the Association of Gas and District Heating Supply Companies (FGW), Profactor GmbH, and the Christof Group. Moreover, the budgets amount to 780 k€ and 850 k€ for EE-Methan aus CO<sub>2</sub> and OptFuel, respectively [207,208].

### 3.18. SoCalGas - P2G Solar Energy Storage

The Southern California Gas Company (SoCalGas) is promoting Power to Gas in the United States with the first demonstrative project of the country that includes methanation. It is focused in enabling higher penetrations of solar power generation through its storage in the natural gas network. The project is located in Golden, Colorado, and scheduled from September 2014 to March 2016 [209].

The research takes place in the laboratories of the National Renewable Energy Laboratory (NREL), where a 150 kW electrolyser produces hydrogen under simulated photovoltaic profiles. The CO<sub>2</sub> is transformed through biological methanation by single-cell methanogens in a liquid media reactor. Then, the product gas is used to produce electricity in a fuel cell [210].

The project is a joint research between SoCalGas, NREL and Electrochaea with a total budget of 900 k\$ equally co-funded [97,209]. In the future, SoCalGas intends to construct a pre-commercial demonstrator of 1 MW [210].

### 3.19. Paul Scherrer Institute – RENERG<sup>2</sup>

The RENERG<sup>2</sup> project (Renewable Energies for Future Energy Supply) focuses on transferring renewable energy surplus to mobility sector, studying electrolysis, methanation, combustion fundamentals, refueling and economics. The project began in 2013 and will be concluded by the end of 2016 [211,212,213].

Methanation research is conducted by the Paul Scherrer Institute through its bubbling fluidized bed methanator (GanyMeth), commissioned in April 2015 and placed in Switzerland. The reactor bed is 2 m high with a diameter of 21 cm, withstanding pressures between 1 and 12 bar and producing up to 160 kW of SNG [214].

Experiments include dynamic load changes and feed gas variations for acting as a polygeneration of fuel, heat and electricity [212]. First tests utilize bottled gas that will be changed for real gases and a 100 kW PEM electrolyser when available. Expected results concern kinetics, hydrodynamics, catalyst abrasion and heat transfer [214].

The project consortium includes EMPA, the Swiss Federal Institute of Technology Zurich (ETH Zurich), the Zurich University of Applied Sciences (ZHAW), and EPFL. Budget amounts around 240 k€, funded by the Competence Centre for Energy and Mobility (CCEM) [212,213].

### 3.20. EMPA – catalytic methanation of industrially-derived CO<sub>2</sub>

The Swiss Federal Laboratories for Materials Science and Technology study the sorption enhanced methanation, which improves CO<sub>2</sub> conversion by absorbing water in situ through a zeolite-nickel catalyst [215,216]. The process and reactor have been developed throughout three different projects focused on catalyst development (HyTech) [212], biogas upgrading (SmartCat) [217], and CO<sub>2</sub> methanation (Catalytic methanation of industrially-derived CO<sub>2</sub>) [218].

Experiments are performed in a stainless steel reactor 45 cm long and 1.8 cm in diameter, operating at 1.2 bar with 13 g of catalyst. The space velocity is 1000 h<sup>-1</sup> that corresponds to an output of 1 kW [215,216,219]. Currently, they evaluate the utilization of CO<sub>2</sub> from the cement industry, and the issues of catalyst deactivation due to sulphur compounds, under the framework of the last mentioned project [218]. Moreover, the Laboratoire de photonique et interfaces of the Swiss Federal Institute of Technology in Lausanne (EPFL-LPI) assesses the

production of renewable hydrogen through photo-electrochemical water splitting in a parallel project. Both lines of work belong to a collaborative joint of 5 individual projects that also covers fuel cells development and sustainability analyses (Joint project CO<sub>2</sub> Reduction & Use: Renewable fuels for efficient electricity production) [220].

EMPA has collaborated, throughout methanation projects, with ZHAW, EPFL and Zeochem AG [212,220,221]. The funds for the experimental facility came from the Swiss Federal Office of Energy (SmartCat project) and the SNSF (Catalytic methanation of industrially-derived CO<sub>2</sub> project) [216].

### 3.21. BTU – CO<sub>2</sub>-methanation of flue gas

The Brandenburg University of Technology (BTU) researches on the methanation of oxyfuel CO<sub>2</sub>, conventional flue gas, and underground-stored CO<sub>2</sub>, besides studying the influence of contaminants like SO<sub>x</sub> or NO<sub>x</sub>. Their last project (CO<sub>2</sub>-Methanation of flue gas), which concluded in October 2015, included a 3 month trial operation at Schwarze Pumpe power plant, in Germany [222,223].

The Power to Gas pilot consists of two parallel methanators which are 153 mm in diameter, 870 mm high and have 15 slots for temperature measurements [224]. Total volume reactor amounts to 30 dm<sup>3</sup> and contains up to 2 kg of catalyst (Ni 66%w on Silica/Alumina). The pilot plant works at 350 °C and 10 bar, with an input capacity of 1200 Nm<sup>3</sup>/day thus producing about 200 Nm<sup>3</sup>/day of CH<sub>4</sub> [225]. H<sub>2</sub> is supplied from bottles although it was proposed the implementation of a PEM electrolyser in the future [224]. Results show conversions above 80% and selectivity between 90% and 100% [225].

Panta Rhei GmbH and Vattenfall Europe Generation AG joined as partners, whilst the BMWi supported the project with 565 k€ [223,226]. Previously, the Brandenburg University of Technology accomplished three projects concerning lab scale tests and upscaling:

- GeoEn (2011–2013): As part of this project, BTU studied the stability of catalysts against SO<sub>x</sub> and NO<sub>x</sub> in the context of oxyfuel process [227]. The lab facility consists of a reactor tube, 8 mm in diameter and 100 mm in length, mounted into an oven that supplies homogeneous temperature distribution during reaction. As catalysts, they used NiO supported on silica gel and RuO<sub>2</sub> on alumina. BMBF supported financially the joint research in which also participated the German Research Centre for Geosciences (GFZ) and the University of Potsdam [228,229].
- CO<sub>2</sub> catalysis, pilot plant I & II (2011–2014): During this two-phase project, the BTU upgraded the lab facility into the pilot plant employed later in their research [225,230]. The project was funded with about 605 k€ from the European Regional Development Fund through the Ministerium für Wissenschaft, Forschung und Kultur (MWFK) [231].

### 3.22. Columbia University – dual function materials for CO<sub>2</sub> capture and conversion

The Columbia University in the City of New York, with financial support from BASF, researches on dual function materials that capture CO<sub>2</sub> from an emission source and convert it to synthetic natural gas in the same reactor and at the same temperature, by using renewable H<sub>2</sub> [232].

The related publications range from 2013 to 2015 covering the process parameters, cyclic stability tests, and kinetic characterization of methanation through a 10% Ru/γ-Al<sub>2</sub>O<sub>3</sub> catalyst [233,234], in addition to feasibility studies of the dual function material consisting of 1–11% w Ru and 1–10%w CaO dispersed on γ-Al<sub>2</sub>O<sub>3</sub> carrier [232]. As methanator they used a fixed bed glass reactor with an inner diameter of 12 mm at a pressure of 1 atm [234].

**Table 3**  
Technical parameters of PtG projects with catalytic methanation.

Project Name	Reactor	Temperature [°C]	Pressure [bar]	Electrolyser [kWe]	Electrolyser Technology	Efficiency PtG [%]	Output [N m <sup>3</sup> /h]	Methane content [%]	Ref.
Audi e-gas	Isothermal fixed bed	–	–	6000	Alkaline	54	325.0	–	[74,77]
HELMETH	–	300	30	15	SOEC	–	5.4	–	[116,123]
MeGa-stoRE – Methane Gas storage of Renewable Energy	Air-cooled	270	8	–	Bottled hydrogen	–	–	97.0–99.0	[139]
RENOVAGAS	Multichannel	275–330	25	15	Alkaline	–	2.0	–	[146,147]
P2G project	Fixed bed	150–700	8–15	7	PEM	–	–	–	[148,151]
Synthetic methane: a medium for storage and transportation of excess renewable energy	–	230–240	6	n/a	Bottled hydrogen	–	–	–	[153,156,157]
DemoSNG	Honeycomb	< 300	–	n/a	PEM	–	–	–	[160,163]
Storage of electric energy from renewable sources in the natural gas grid – water electrolysis and synthesis of gas components	Fixed bed / Slurry	–	–	6	PEM	–	–	–	[165,167]
CO <sub>2</sub> -SNG	Structured	–	–	–	–	–	–	–	[170,173,174]
CO <sub>2</sub> recycling via reaction with hydrogen	Fixed bed	300–350	–	5	PEM	–	–	–	[175,176]
Kommunale Kläranlagen als Energiespeicher	Isothermal	335	–	312	–	–	59.0	–	[184,185,186]
CO <sub>2</sub> Conversion to Methane Project	Fixed bed	200	–	n/a	Alkaline	–	1000.0	–	[188,190]
Pilot plant – Tohoku Institute of Technology	–	–	–	n/a	Alkaline	–	1	–	[194,195]
Prototype plant – Tohoku University	–	–	–	n/a	Alkaline	–	–	–	[194,195]
EE-Methan from CO <sub>2</sub> Catalytic methanation of industrially-derived CO <sub>2</sub>	Honeycomb Fixed bed	> 350	1–20	–	–	–	3	–	[198,203,204]
SmartCat	–	–	–	–	Bottled hydrogen	–	–	–	[217,219]
HyTech	–	–	–	–	Bottled hydrogen	–	–	–	[212]
CO <sub>2</sub> -Methanation of flue gas	Fixed bed	350	10	–	Bottled hydrogen	–	200	–	[223,224,226]
CO <sub>2</sub> catalysis, pilot plant - Technikum 1 & 2	Fixed bed	–	–	–	Bottled hydrogen	–	–	–	[226,231]
GeoEn	Fixed bed	–	–	–	Bottled hydrogen	–	–	–	[228,229,230]
Dual function materials for CO <sub>2</sub> capture and conversion using renewable H <sub>2</sub>	Fixed bed	–	1	–	Bottled hydrogen	–	–	–	[233,234,235]

### 3.23. BTU-FESPE – biocatalytic methanation in an anaerobic three-phase system

The Faculty of Environmental Science and Process Engineering of the Brandenburg University of Technology (BTU-FESPE) has developed an anaerobic trickle-bed reactor for biocatalytic methanation at 37 °C and ambient pressure in a continuous process. Their last prototype includes an electrolyser for H<sub>2</sub> generation and conventional CO<sub>2</sub>-pressure cylinders, although it can also enrich a biogas source [235].

The reactor is 141 cm in length and 28.2 cm in diameter, with a total volume of 88 L. It contains a fixed-bed of random packing material with a high specific surface area on which microorganisms can be immobilized and surrounded by gas phase. Then, they are sprinkled with liquid thus creating greater concentration gradients and

improving the driving force for the mass transfer. Results show methane outputs of 98% in a single reactor without necessity for gas recirculation [235].

Once the detailed information has been described for each individual PtG project, the technical information is filtered and presented in the following tables to facilitate the comparison between operation parameters. Table 3 includes those projects in which CO<sub>2</sub> methanation is carried out through a catalytic process.

The projects with a biological methanation stage are gathered in Table 4 where their most relevant technical parameters are summarized.

The projects in Table 2 which are not included in Tables 3 or 4 correspond to those projects whose methanation process is not clearly defined in open literature.

**Table 4**  
Technical parameters of PtG projects with biological methanation.

Project Name	Reactor	Temperature [°C]	Pressure [bar]	Electrolyser [kWe]	Electrolyser Technology	Output [N m <sup>3</sup> /h]	Methane content [%]	Ref.
POWERSTEP	–	–	–	–	–	–	–	[97,104,105]
P2G-BioCat project	Liquid phase	60–65	–	1000	Alkaline	–	–	[90,94,96]
Pre-commercial	Liquid phase	–	–	250	PEM	–	–	[100,102]
Industrial Biogas Test	–	–	–	1	–	–	–	[99,100]
BioPower2Gas	–	–	–	300	PEM	–	–	[107,108,109]
Mikrobielle Methanisierung	–	–	–	180	PEM	–	–	[114,115]
Power-to-Gas im Eucolino	Liquid phase	–	–	120	–	5.3	75.0	[73,112]
Biological methanation of pure streams	–	40–65	–	55	–	–	–	[73]
SYMBIO	Anaerobic digester	–	–	–	–	–	–	[143,145]
OptFuel	–	–	–	–	–	–	–	[199,204,207]
P2G Solar Energy Storage RD & D	Liquid phase	–	–	150	–	–	–	[209,210]
Biocatalytic methanation in an anaerobic three-phase system	Anaerobic trickle-bed	37	1	–	–	–	98.0	[235,236]

#### 4. Conclusions

Because of worldwide renewable energy penetration targets, massive energy storage concepts have taken significance during recent years. Power to Gas seems to tackle this issue not only in terms of energy storage but also in CO<sub>2</sub> utilization. A large number of researchers has revisited PtG technology in the last decade with energy storage purposes to better integrate renewable sources in the system. A remarkable increase in technology deployment in terms of ongoing projects dealing with 3step-PtG processes started after 2010 and currently available information predicts that this period will last, at least, until 2025.

Although the first pilot plant was erected in Japan, the current leadership holds in Europe, mainly thanks to the support of the governments of Germany, Denmark and Switzerland. These experiences combine pilot and demonstration plants whose electrolyser sizes vary from few kW<sub>e</sub> (lab-scale plants) to 3×2.0 MW<sub>e</sub> (largest existing plant). USA has also contributed to the deployment of the technology with up to four projects since 2009. Data show that the average budgets for demo-plants projects are around one million euro per year in most cases.

Regarding methanation technologies, large projects cover mainly catalytic processes due to its scale up capability, although recently some biological projects also rose up to the MW range. Current pilot

plants prefer biogas as source of CO<sub>2</sub> since the energy penalty associated to carbon capture vanishes. For the same reason, syngas upgrading emerges as a future suitable option. Few others have experienced with more innovative CO<sub>2</sub> sources such as industrial processes, the atmosphere, natural gas extraction processes or wastewater treatment plants.

There is large room for further investigation to address the real potential of this technology as a system for decarbonizing natural gas. Future research must focus on the study of new sources of CO<sub>2</sub> which present low energy penalty and a renewable origin in order to completely close the CO<sub>2</sub> cycle. Furthermore, it must be tackled the current high costs of this kind of systems, and the necessity of optimize the heat management for a possible cogeneration or trigeneration integration that increases the global efficiency of the process.

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#### Annex A. List of institutions/companies and abbreviations

Abbreviation	Institution
AAU	Aalborg University
AB InBev	Anheuser-Busch InBev NV/SA
Abengoa	Abengoa Hidrógeno
AGH-UST	AGH University of Science and Technology
AgroPark	Agro Business Park A/S
APS	Aqua Plant Solutions GmbH
Arctik	Arctik SPRL
Atemis	Atemis GmbH
Atmostat	Atmostat
AU	Aarhus University
AU Herning	Aarhus University Department of Business Development and Technology

<i>Audi</i>	Audi AG
<i>Avedøre-WWTP</i>	Avedøre Wastewater Treatment Plant
<i>AVL</i>	AVL GmbH
<i>BASF</i>	BASF
<i>BEE</i>	Bau- und Entsorgungsbetrieb Emden
<i>BFP</i>	Studio Tecnico BFP srl
<i>Biofos</i>	Biofos A/S
<i>BMBF</i>	Federal Ministry of Education and Research
<i>BMUB</i>	Federal Ministry for the Environment, Nature Conservation, Building and Nuclear Safety
<i>BMWFJ</i>	Bundesministeriums für Wirtschaft, Familie und Jugend
<i>BMWi</i>	Federal Ministry for Economic Affairs and Energy
<i>BTU</i>	Brandenburg University of Technology
<i>BTU-FESPE</i>	Faculty of Environmental Sciences and Process Engineering of the Brandenburg University of Technology
<i>BWB</i>	Berliner Wasserbetriebe
<i>Carbotech</i>	Carbotech
<i>CAS</i>	Chinese Academy of Science
<i>CCEM</i>	Competence Centre for Energy and Mobility
<i>CEA</i>	Atomic Energy and Alternative Energies Commission
<i>Cemtec</i>	Cemtec
<i>Chalmers</i>	Chalmers University of Technology
<i>Christof Group</i>	Christof Group
<i>Climeworks</i>	Climeworks
<i>CNH2</i>	National Centre for Hydrogen and Fuel Cell Technology
<i>Columbia University</i>	The Columbia University in the City of New York
<i>Cortus</i>	Cortus
<i>CUBE</i>	CUBE
<i>DAE</i>	Daiki Ataka Engineering Co., Ltd.
<i>DBFZ</i>	German Biomass Research Centre
<i>DBI-GUT</i>	DBI Gas-und Umwelttechnik GmbH
<i>DEA</i>	Danish Energy Agency
<i>DGC</i>	Danish Gas Technology Centre
<i>DNV GL</i>	DNV GL Group
<i>DONG</i>	DONG Energy
<i>DRI</i>	Desert Research Institute
<i>DTU</i>	Technical University of Denmark
<i>DTU-Environment</i>	Technical University of Denmark - Department of Environmental Engineering
<i>DTU-Mekanik</i>	Technical University of Denmark - Department of Mechanical Engineering
<i>DVGW</i>	Deutscher Verein des Gas- und Wasserfaches e.V.
<i>DVGW-EBI</i>	Deutscher Verein des Gas- und Wasserfaches e.V. Forschungsstelle at the Engler-Bunte Institute of KIT
<i>E.ON</i>	E.ON AG
<i>Ea</i>	Ea Energianalyse A/S
<i>EAM EnergiePlus</i>	EAM EnergiePlus GmbH
<i>Eawag</i>	Swiss Federal Institute of Aquatic Science and Technology
<i>ECN</i>	Energy Research Centre of the Netherlands
<i>EDI</i>	Energy Delta Institute
<i>EII Spa</i>	Engineering Ingegneria Informatica SPA
<i>Electrochaea</i>	Electrochaea GmbH
<i>Elplatek</i>	Elplatek A/S
<i>EMPA</i>	Swiss Federal Laboratories for Materials Science and Technology
<i>Enagas</i>	Enagás S.A.
<i>EnBW</i>	Energie Baden-Württemberg AG
<i>Energie 360°</i>	Energie 360° AG
<i>EnergieNetz</i>	EnergieNetz Mitte GmbH
<i>EnergiMidt</i>	EnergiMidt
<i>Energinet.dk</i>	Energinet.dk
<i>Energy Valley</i>	Stichting Energy Valley
<i>EPFL</i>	Swiss Federal Institute of Technology in Lausanne
<i>EPFL-CEN</i>	Energy Centre of the Swiss Federal Institute of Technology in Lausanne
<i>EPFL-IPESSE</i>	Industrial Process and Energy Systems Engineering of the Swiss Federal Institute of Technology in Lausanne
<i>EPFL-LMER</i>	Laboratory of Materials for Renewable Energy of the Swiss Federal Institute of Technology in Lausanne
<i>EPFL-LPI</i>	Laboratoire de photonique et interfaces of the Swiss Federal Institute of Technology in Lausanne
<i>Erdgas Obersee</i>	Erdgas Obersee AG
<i>Erdgas Regio</i>	Erdgas Regio AG
<i>ERIC</i>	European Research Institute of Catalysis AISBL
<i>ETH Zurich</i>	Swiss Federal Institute of Technology Zurich
<i>ETOGAS</i>	ETOGAS GmbH

<i>EWE Biogas</i>	EWE Biogas GmbH & Co. KG
<i>EWJR</i>	Elektrizitätswerk Jona-Rapperswil AG
<i>EWZ</i>	Elektrizitätswerk der Stadt Zürich
<i>FCC-Aqualia</i>	FCC-Aqualia S.A.
<i>FENES</i>	Research Centre for Power Grids and Energy Storage
<i>FFG</i>	Austrian Research Promotion Agency
<i>FGW</i>	Association of Gas and District Heating Supply Companies
<i>Fraunhofer IPM</i>	Fraunhofer Institute for Physical Measurement Techniques
<i>Fraunhofer ISE</i>	Fraunhofer Institute for Solar Energy Systems
<i>Fraunhofer IWES</i>	Fraunhofer Institute for Wind Energy and Energy System Technology
<i>GA-Group</i>	Gesellschaft für Abwasserberatung und Management mbH
<i>Gas Natural Fenosa</i>	Gas Natural Fenosa
<i>GFZ</i>	German Research Centre for Geosciences
<i>GreenHydrogen</i>	GreenHydrogen.dk
<i>Haldor Topsoe</i>	Haldor Topsoe A/S
<i>Hanze UAS</i>	Hanze University of Applied Sciences
<i>HBFZ</i>	Hessian Biogas Research Centre
<i>HIRC</i>	Hydrogen Innovation & Research Centre
<i>Hitachi Zosen</i>	Hitachi Zosen Corporation
<i>HMN Gashandel</i>	HMN Gashandel A/S
<i>HMN Naturgas</i>	HMN Naturgas I/S
<i>HMUELV</i>	Hessian Ministry of the Environment, Climate Protection, Agriculture and Consumer Protection
<i>Hokudai</i>	Hokkaido University
<i>HS Emden/Leer</i>	Hochschule Emden/Leer
<i>HS Emden/Leer-EUtec</i>	Emder Institute of Environmental Engineering of the Hochschule Emden/Leer
<i>HSR</i>	Hochschule für Technik Rapperswil
<i>HSR-IET</i>	Institute for Energy Technology of the Hochschule für Technik Rapperswil
<i>H-Tec</i>	H-Tec Systems
<i>Hydrogenics</i>	Hydrogenics
<i>ibis Umwelttechnik</i>	ibis Umwelttechnik GmbH
<i>ICHPW</i>	Institute for Chemical Processing of Coal
<i>ICP-CSIC</i>	Institute of Catalysis and Petrochemistry
<i>IdE</i>	Institute decentralised Energy Technologies
<i>IMR</i>	Institute for Materials Research of the Tohoku University
<i>INBIOM</i>	Innovation Network For Biomass
<i>INSA</i>	Institut national des sciences appliquées de Rouen
<i>Insero</i>	Insero Business Services
<i>IoLiTec</i>	Ionic Liquids Technologies GmbH
<i>JKU Linz</i>	Johannes Kepler University Linz
<i>JKU Linz-EI</i>	Energy Institute of the Johannes Kepler University Linz
<i>Juwi</i>	Juwi AG
<i>KIT</i>	Karlsruhe Institute of Technology
<i>KTH</i>	KTH Royal Institute of Technology
<i>KWB</i>	Berlin Centre of Competence for Water
<i>Lemvig Biogas</i>	Lemvig Biogas Amba
<i>Maabjerg BioEnergy</i>	Maabjerg BioEnergy A/S
<i>MES</i>	Mitsui Engineering and Shipbuilding Co.
<i>MicroEnergy</i>	MicroEnergy GmbH
<i>MINECO</i>	Ministry of Economy and Competitiveness
<i>MIT</i>	Massachusetts Institute of Technology
<i>MU Leoben</i>	University of Leoben
<i>MWFK</i>	Ministerium für Wissenschaft, Forschung und Kultur
<i>MWK</i>	Ministerium für Wissenschaft und Kultur
<i>NEAS</i>	NEAS Energy
<i>NGF</i>	Naturgas Fyn I/S
<i>NREL</i>	National Renewable Energy Laboratory
<i>NRIM</i>	National Research Institute for Metals
<i>NTUA</i>	National Technical University of Athens
<i>NU</i>	Northwestern University
<i>Outotec</i>	Outotec
<i>ÖVGW</i>	Austrian Association for Gas and Water
<i>Panta Rhei</i>	Panta Rhei GmbH
<i>PlanEnergi</i>	PlanEnergi.dk
<i>PoliTo</i>	Politecnico di Torino
<i>Profactor</i>	Profactor GmbH
<i>PSI</i>	Paul Scherrer Institute

<i>PTTEP</i>	PTT Exploration and Production Public Company Limited
<i>Rafako</i>	Rafako S.A.
<i>RCO2 AS</i>	RCO2 AS
<i>Regio Energie</i>	Regio Energie Solothurn
<i>RUG</i>	University of Groningen
<i>Ryoka</i>	Ryoka Matthey Corporation
<i>SCCER-HaE</i>	Swiss Competence Centre for Energy Research - Heat and Electricity Storage
<i>Schmack</i>	Schmack Biogas GmbH
<i>SDU</i>	University of Southern Denmark
<i>SFOE</i>	Swiss Federal Office of Energy
<i>SNSF</i>	Swiss National Science Foundation
<i>SoCalGas</i>	Southern California Gas Company
<i>Stadtwerke Emden</i>	Stadtwerke Emden GmbH
<i>Stedin</i>	Stedin
<i>StMWi</i>	Bavarian Ministry of Economic Affairs, Infrastructure, Transport and Technology
<i>Sunfire</i>	Sunfire GmbH
<i>Sustec</i>	Sustec Consulting & Contracting BV
<i>Tauron</i>	Tauron Group
<i>Tecnia</i>	Tecnia
<i>Thalen Consult</i>	Thalen Consult GmbH
<i>TKI Gas</i>	TKI Gas
<i>TMLFUN</i>	Thuringian Ministry for Agriculture, Forestry, Environment and Nature Conservation
<i>Tohoku University</i>	Tohoku University
<i>TohTech</i>	Tohoku Institute of Technology
<i>TS-Torino</i>	Turbo Service Torino spa
<i>TU Berlin</i>	Technische Universität Berlin
<i>TU Wien</i>	Vienna University of Technology
<i>TU-Delft</i>	Delft University of Technology
<i>UBA</i>	Umweltbundesamt
<i>Uchicago</i>	The University of Chicago
<i>UM</i>	University of Montreal
<i>UM-DMI</i>	University of Montreal - Department of Microbiology and Immunology
<i>Uni-Postdam</i>	University of Potsdam
<i>Uni-Regensburg</i>	Universität Regensburg
<i>Vattenfall</i>	Vattenfall Europe Generation AG
<i>Veolia</i>	Veolia Deutschland GmbH
<i>Veolia-WT</i>	Veolia Water Technologies AB
<i>Viessmann</i>	Viessmann Group
<i>VSG</i>	Verband der Schweizerischen Gasindustrie
<i>WT &amp; T Polska</i>	West Technology & Trading Polska Sp. Z o. o.
<i>Xergi</i>	Xergi A/S
<i>Zeochem</i>	Zeochem AG
<i>ZHAW</i>	Zurich University of Applied Sciences
<i>ZSW</i>	Centre for Solar Power and Hydrogen Research Baden-Württemberg
<i>ZVKSW</i>	Zweckverband Verbandskläranlage Schwandorf-Wackersdorf

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