Energy Storage as Part of a Secure Energy Supply

Florian Ausfelder[1,],*, Christian Beilmann[2], Martin Bertau[3], Sigmar Bräuninger[4], Angelika Heinzel[5], Renate Hoer[6], Wolfram Koch[6], Falko Mahlendorf[5], Anja Metzelthin[7], Marcell Peuckert[8], Ludolf Plass[9], Konstantin Räuchle[3], Martin Reuter[10], Georg Schaub[11], Sebastian Schiebahn[12], Ekkehard Schwab[4], Ferdi Schüth[13], Detlef Stolten[14], Gisa Teßmer[15], Kurt Wagemann[1], Karl-Friedrich Ziegahn[7,16]

Abstract

The current energy system is subject to a fundamental transformation: A system that is oriented towards a constant energy supply by means of fossil fuels is now expected to integrate increasing amounts of renewable energy to achieve overall a more sustainable energy supply. The challenges arising from this paradigm shift are currently most obvious in the area of electric power supply. However, it affects all areas of the energy system, albeit with different results. Within the energy system, various independent grids fulfill the function of transporting and spatially distributing energy or energy carriers, and the demand-oriented supply ensures that energy demands are met at all times. However, renewable energy sources generally supply their energy independently from any specific energy demand. Their contribution to the overall energy system is expected to increase significantly. Energy storage technologies are one option for temporal matching of energy supply and demand. Energy storage systems have the ability to take up a certain amount of energy, store it in a storage medium for a suitable period of time, and release it in a controlled manner after a certain time delay. Energy storage systems can also be constructed as process chains by combining unit operations, each of which cover different aspects of these functions. Large-scale mechanical storage of electric power is currently almost exclusively achieved by pumped-storage hydroelectric power stations. These systems may be supplemented in the future by compressed-air energy storage and possibly air separation plants. In the area of electrochemical storage, various technologies are currently in various stages of research, development, and demonstration of their suitability for large-scale electrical energy storage. Thermal energy storage technologies are based on the storage of sensible heat, exploitation of phase transitions, adsorption/desorption processes, and chemical reactions. The latter offer the possibility of permanent and loss-free storage of heat. The storage of energy in chemical bonds involves compounds that can act as energy carriers or as chemical feedstocks. Thus, they are in direct economic competition with established (fossil fuel) supply routes. The key technology here – now and for the foreseeable future – is the electrolysis of water to produce hydrogen and oxygen. Hydrogen can be transformed by various processes into other energy carriers, which can be exploited in different sectors of the energy system and/or as raw materials for energy-intensive industrial processes. Some functions of energy storage systems can be taken over by industrial processes. Within the overall energy system, chemical energy storage technologies open up opportunities to link and interweave the various energy streams and sectors. Chemical energy storage not only offers means for greater integration of renewable energy outside the electric power sector, it also creates new opportunities for increased flexibility, novel synergies, and additional optimization. Several examples of specific energy utilization are discussed and evaluated with respect to energy storage applications.

The article describes various technologies for energy storage and their potential applications in the context of Germany's Energiewende, i.e. the transition towards a more sustainable energy system. Therefore, the existing legal framework defines some of the discussions and findings within the article, specifically the compensation for renewable electricity providers defined by the German Renewable Energy Sources Act, which is under constant reformation. While the article is written from a German perspective, the authors hope this article will be of general interest for anyone working in the areas of energy systems or energy technology.

Keywords: Energy storage technology, Energy supply, Optimization

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Table of Contents

1 Introduction

1.1 Demands on the Energy Supply

A secure energy supply is one of the basic requirements of a modern economy. The goal is to ensure an affordable and reliable energy supply for residential, commercial, and industrial consumers. A modern energy system should minimize the emission of greenhouse gases and through its price structure also be attractive for energy-intensive companies in international competition.

These requirements result in a series of measures to address the challenges. For the smoothest possible supply of energy, the provision and demand-oriented expansion of cost-effective, high-performance, and efficient energy infrastructure, i.e., primarily the supply grids, are indispensable. The strategic reserves of conventional fuels are able to cover short- and medium-term supply shortages and guarantee stable primary supply. Diversification of energy sources, carriers, and providers makes the energy supply more resistant to political changes. The increased use of renewable energy leads to an even more sustainable energy supply due to the lower consumption of fossil raw materials and the consequent reduction in emissions of greenhouse gases.

Energy supply and consumption must be balanced spatially and temporally. The former is achieved through transport, transmission, and distribution grids, which ensure demand-oriented, comprehensive, and trouble-free supply of consumers with the required energy or energy carrier. The grids with their international connections allow demand and supply to be balanced by importing missing and exporting excess energy.

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[1] Dr. Florian Ausfelder (corresponding author), Prof. Dr. Kurt Wagemann
DECHEMA Gesellschaft für Chemische Technik und Biotechnologie e.V., Theodor-Heuss-Allee 25, 60486 Frankfurt am Main, Germany.
E-Mail: ausfelder@dechema.de

[2] Dr. Christian Beilmann
Helmholtz Gemeinschaft, Anna-Louisa-Karsch Strasse 2, 10178 Berlin, Germany.

[3] Prof. Dr. Martin Bertau, Dr. Konstantin Räuchle
Technische Universität Bergakademie Freiberg, Akademiestrasse 6, 09599 Freiberg, Germany.

[4] Dr. Sigmar Bräuninger, Dr. Ekkehard Schwab
BASF SE, Carl-Bosch-Strasse 38, 67063 Ludwigshafen, Germany.

[5] Prof. Dr. Angelika Heinzel, Dr. Falko Mahlendorf
Universität Duisburg-Essen, Forsthausweg 2, 47057 Duisburg, Germany.

[6] Dr. Renate Hoer, Prof. Dr. Wolfram Koch
GDCh Gesellschaft Deutscher Chemiker e.V., Varrentrappstrasse 40–42, 60486 Frankfurt am Main, Germany.

[7] Dr. Anja Metzelthin, Dr.-Ing. Karl-Friedrich Ziegahn
Deutsche Physikalische Gesellschaft e.V., Hauptstrasse 5, 53604 Bad Honnef, Germany.

[8] Prof. Dr. Marcell Peuckert
Katzenlückstrasse 11, 65719 Hofheim am Taunus, Germany.

[9] Dr. Ludolf Plass
Parkstrasse 11a, 61476 Kronberg im Taunus, Germany.

[10] Dr. Martin Reuter
VCI Verband der Chemischen Industrie e. V., Mainzer Landstrasse 55, 60329 Frankfurt am Main, Germany.

[11] Prof. Dr.-Ing. Georg Schaub
Karlsruher Institut für Technologie, Engler-Bunte-Institut, Engler-Bunte-Ring 1, 76131 Karlsruhe, Germany.

[12] Dr. Sebastian Schiebahn
Lyatenstrasse 3, 52382 Niederzier, Germany.

[13] Prof. Dr. Ferdi Schüth
Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany.

[14] Prof. Dr.-Ing. Detlef Stolten
Forschungszentrum Jülich GmbH, Wilhelm-Johnen-Strasse, 52428 Jülich, Germany.

[15] Dr. Gisa Teßmer
DGMK Deutsche Wissenschaftliche Gesellschaft für Erdöl, Erdgas und Kohle e.V., Überseering 40 (RWE-Haus), 22297 Hamburg, Germany.

[16] Dr.-Ing. Karl-Friedrich Ziegahn
Karlsruher Institut für Technologie, Campus Nord, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.

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While grids ensure the local distribution of energy or fuels, energy storage systems contribute to making energy available on demand. They can temporarily absorb excess energy or energy sources and make them available again later. A temporary excess of one form of energy can be transformed into another, which can then be used or stored. However, conversion losses must be taken into account.

The existing energy storage systems are sufficient for the current structure of the energy system. Strategic stockpiling of oil and gas can compensate temporary bottlenecks in transport, power plants, and heat supply. Pumped-storage hydroelectric power stations in combination with flexible operation of power plants can adequately respond to fluctuations in electricity consumption. However, the increasing expansion of renewable energy with feed-in priority, the dependency relationships in the supply of energy sources, and new concepts of mobility suggest an important role for energy storage systems in the medium term. Energy storage can therefore be characterized as an important, but not urgent problem. Nevertheless, research and development are already required now to be prepared for the time when energy storage is needed on a larger scale.

The fact that we are currently able to cope with the existing energy storage systems cannot be taken as granted for the future. Instead, it provides the opportunity and an obligation to future generations to initiate the necessary developments with the aim of moving to a sustainable energy system.

Energy storage systems are a possible, and sometimes crucial option for dealing with a fluctuating energy supply. However, they are not the only way to respond to fluctuations in supply. The forecasts for the earnings from renewable energy sources are becoming more accurate and allow for improved coordination and more efficient use. Additionally, the demand side can be addressed to provide a contribution to system stability. The availability of spare generation capacity is another way to meet demand even in times of low supply of renewable energy. Finally, a higher-performance grid can compensate for local temporal variations by transport to and from other regions.

In the spirit of a forward-looking energy policy that develops options and is open to flexible implementation, the scientific and technological development of energy storage systems should currently be pursued in order to have this option available when it is needed.

2 Overall Concept of the Energy System

2.1 Structure of the German Energy System

The use of primary energy in Germany covers three major areas of need. With around 50 % of the final energy consumption, the heating market represents the largest share [1], whereby mainly natural gas and fuel oil are used as energy sources. In second place, the use of petroleum derivatives such as gasoline, diesel fuel, and kerosene in the transport sector follows. In third place is the use of electricity, generated by coal, gas, nuclear and renewable sources. All of these fuels and their usage forms are made available to the consumer through conversion and supply systems. Thereby the challenge is to provide the energy needed in the right form at any time and any place. Currently, the energy system in Germany is still dominated by fossil fuels, but the contribution of renewable energy is rising steadily, especially in the electricity sector.

2.2 Integration of Renewable Energies into the Energy Supply

Germany places strong emphasis on the development of renewable energy. The central objective is to build a sustainable energy system by reducing the emission of greenhouse gases (especially CO_2). Furthermore, the dependence on unreliable suppliers should be reduced and the expected price increases of fossil fuels should partially be offset. The assumption of increased fossil fuel prices has been the basis of many scenarios for implementation of renewable energies. However, within recent past, this trend could not be observed and the challenge of a transformation towards a more renewable energy supply has likely to be met with low prices of fossil fuels in the future.

In particular in the area of power supply, the increased feed-in of renewable energies that are not suitable for meeting base-load requirements leads to increased exchange and a greater coordination of activities with neighboring countries. Also, the reduction of emission of greenhouse gases is currently not achievable because old coal-fired power plants with a relatively high output of CO_2 can be operated more economically than modern gas-fired power plants. The reason is the very low price of CO_2 emissions certificates, currently around 5–7 € t^{-1} CO_2 in the European Emissions Trading Scheme (ETS), and the relatively high price of natural gas. The CO_2 balance of power and fuels generated from renewable resources is controversial. The relevant renewable energies are listed in Tab. 1. All renewable energies are subject to geographic restrictions, arising either from the energy conversion technology itself or from its political and social acceptance. Renewable energy can be used centrally or locally.

2.3 Future Structure and Challenges of the Energy Supply

The further expansion of renewable energies is the declared objective of the energy transition. Its realization takes place, besides fixed quotas for biofuels, mainly in the electricity sector through guaranteed purchases at fixed prices. On the basis of the regulations of the German Renewable Energy Sources Act (*Erneuerbare-Energien-Gesetz*: EEG), the related costs are, with some exceptions, transferred to the consumer (EEG surcharge). The increasing expansion of renewable energies is forcing a paradigm shift in the traditional power distribution structures.

The existing electricity system is demand-driven and is supported by fossil and nuclear energy sources in large-scale plants with their own utilities and consumer structure. These changes are most clearly evident in the electricity grid. On the generation side, the classic division into base-load, intermediate, and peak-load supply is becoming increasingly blurred [2].

At the same time, renewable energies cannot provide the necessary guaranteed performance (i.e., electricity generation capacity) that must be available at all times. Owing to the irreg-

Table 1. Overview of the capabilities and limitations of renewable energies.

Parameter / Technology	Base load	Predictability	Geographical limitations	Energy grid connection	Area of Application	Notes
Run-of-river power plants	Yes	Yes	River course	Power grid (transmission and distribution network)	Regional/national	Established technology, repowering
Hydroelectric pumped storage	No	Yes	Altitude difference	Power grid (transmission network)	Regional/national	Established technology, repowering
Onshore wind power	No	Conditionally	Wind yield/ landscape and nature conservation	Power grid (transmission and distribution network)	Regional	Established technology, repowering
Offshore wind power	No	Conditionally	Wind yield/out of sight of the coast	Power grid (transmission network)	National	Ensure grid connection
Photovoltaics	No	Conditionally	Sunlight	Power grid (distribution network)	Regionaocal	Fragmented generation structure
Solar thermal	No	Conditionally	Direct sunlight	No (district heating networks possible)	Local	Fragmented generation structure
Central solar thermal (CSP) with/without steam power plants	Yes (with thermal storage)/ no (without thermal storage)	Conditionally	Direct sunlight	District heating networks, power grid	Regionaocal	Depending on location
Geothermal	Yes	Yes	Geological structure	No (district heating networks possible)	Local	Problematic social acceptance
Biogas with cogeneration plant	Yes	Yes	Cultivated area biomass	Gas network after separation of CO_2	Local	Generation of heat and electricity
Biomass	Yes	Yes	Cultivated area biomass	Power grid, district heating network	Local	Generation of heat and electricity
Biofuels	Yes	Yes	Cultivated area biomass	No, transportation via rail tank cars	National	Vehicles

ular contributions of renewable energy from centralized and decentralized power producers, a greater gap is created between the temporally and locally available generation capacity and the consumer demand. This discrepancy must be eliminated in the most efficient and cost-effective manner.

The heat and mobility sectors (with the exception of electric mobility) as well as energy-intensive industrial processes are currently not in the focus of energy policy measures. Nevertheless, it is recognized that only through the inclusion of these areas can the energy transition be successful, especially with regard to the reduction of CO_2 emissions.

2.4 European Perspective

Energy supply and energy policy that operate only from a national perspective are in danger of ignoring the opportunities that arise through cooperation among national energy systems to build a greater European energy network. Already today, there are far-reaching networks of international energy supply structures. This will further increase in the future, whereby also national strategic interests will significantly influence the energy policy in the medium term. These include, e.g., the preference for domestic energy sources, maintaining a nuclear component, agreements for the supply of natural gas, and regarding the German energy transformation as an exclusively national project.

Indeed, much of the energy infrastructure is already linked throughout Europe, and isolated decisions and actions have an impact on the European partner countries and their energy systems. At the same time, opportunities are created, especially in the use of renewable energy sources, whereby countries can share their geographical advantages and thus can contribute to the security of supply, cost effectiveness, and reducing greenhouse gas emissions from the energy sector. This requires expansion and maintenance of the European energy infrastructure, rules and procedures that enable fair access and secure exchange between stakeholders, and coherence of national and European rules. The European Union addresses this challenge via its Energy Union initiative.

2.5 Definition of Energy Storage

The term "energy storage" has a number of different meanings. It describes both the storage container (e.g., a gas cavern) as well as the storage medium (e.g., hydrogen as energy storage material), in some cases even both (e.g., batteries). Some storage media (especially those that store energy in the form of chemical bonds, e.g., biomass and liquid synthetic fuels) are produced during the storage process and consumed during discharge, while other storage media are preserved (e.g., in batteries). Often, the entire periphery of an energy storage system, which defines the possible applications of the storage system, is also summarized under this term.

In the context of this article, which mainly deals with the function of energy storage systems and their application, the following definition of energy storage is used: An energy storage system is one that can absorb an amount of energy in a controlled manner (loading), store it for a suitable time period in a storage medium (storage), and deliver it in a controlled manner (discharge) at a desired time (cf. the definition proposed by BDEW [3]).

From the above definition, the following consequences, among others, follow:

- The energy forms for charging, storage, and discharging may be different.
- These functions (charging, storage, discharging) may be integrated into one system or be implemented in a process chain of different, spatially separated components.
- If the storage medium is transportable, the discharging can also be performed at a different location and/or being mobile.
- Chemical energy storage is its own storage medium, whereas other forms of energy require an additional storage medium.
- Rechargeability with respect to the storage system, but not necessarily with respect to the storage medium, should be given.
- This definition also includes fossil fuels and biomass.

2.6 Function and Contribution of Power Grids to a Secure Energy Supply

The ability of grids to ensure the transportation and local distribution of energy or energy carriers is central to a balance between energy supply and consumption, which is one of the basic requirements of efficient energy use. Each of the possible energy supply grids has its own infrastructure that is tailored to the grid-specific functions. To date, the requirements of the grids were often considered separately. In this context, a report by the *Bundesnetzagentur* (Federal Network Agency) in May 2012 [4] pointed out the critical link between electricity and gas supply. In a recent study by the Fraunhofer ISE [5], the possibility of an energy supply based nearly entirely on renewable energy by 2050 is outlined, which depends largely on the combination of heat and electricity supply.

At present, it is still difficult to sufficiently estimate the synergies that could result from better interlinking between different grids. For the purposes of supply security and flexibility, these intergrid links should be regarded as an opportunity, because they open up the possibility of combining the individual advantages of the respective grids and forms of energy. Smart combination and a systematic approach could result in a more cost-effective potential for energy efficiency than isolated consideration of each energy form. In the following, the existing energy grids are briefly summarized.

2.6.1 Electricity Grid

Grid structure: EU, national (high-voltage grid, 220–380 kV), regional (medium-voltage grid), local (low-voltage grid).
Grid function: Secure supply of electricity to private, commercial, industrial, and institutional consumers.
Storage technologies: Hydroelectric pumped storage power plants (commercialized), diabatic (one plant) and adiabatic compressed-air energy storage (dormant demonstration project), batteries (an energy reservoir based on Li-ion batteries has been connected to the grid in Schwerin).
Function of storage: Improved load management and grid stabilization, peak shaving, load leveling by providing positive and negative regulation energy for balancing production and consumption, especially with respect to the favored supply of renewable energies unsuitable for base-load supply.
Notes: The grid fulfills primarily a transport function. The power grid itself has no storage capacity. The rotating masses of conventional power plants can be understood as flywheel accumulators, albeit with the same restrictions of low energy storage density.

Improved load management reduces peak prices and fluctuations, which worsens the economic conditions for the implementation of new storage systems with increasing storage capacity. Other measures for grid stabilization include consumption control (consumer) as well as import and export of electricity, EU-wide grid development (especially nodes), and enhanced mutual coordination. Economically, it is probably wise to combine different grid stabilization measures in a structured fashion. This raises questions regarding the connections and regulation of the market. An expansion of network structures at national and international levels reduces the economic efficiency and the need for storage systems. Fig. 1 illustrates the high-voltage grid in Germany, while Fig. 2 shows schematically the relationship between the different voltage levels.

2.6.2 Gas Grid

Grid structure: EU, national, regional, local.
Grid function: Secure supply of natural gas to consumers.
Storage technologies: Cavern and pore storage, grid capacity, supply of purified biogas, possible feeding of H_2 (research, development, and demonstration). Capacity (working gas volume) of pore storage: 9.8 billion m^3, cavern storage: 14.3 billion m^3. The storage capacity covers approximately 20 % of the annual consumption in Germany, which is highly

Figure 1. Map showing the 220/380-kV lines of the German high-voltage grid. © Forum Network Technology/Network Operation in the VDE (FNN) 2016, VDE Association for Electrical, Electronic & Information Technologies [6]. The other power levels are too fragmented to be displayed clearly in this figure. Solid lines: existing power lines; dashed lines: power lines under construction; dotted lines: projected power lines; magenta lines: high voltage direct current power lines; filled dots: power transformation stations; open dots: large cities.

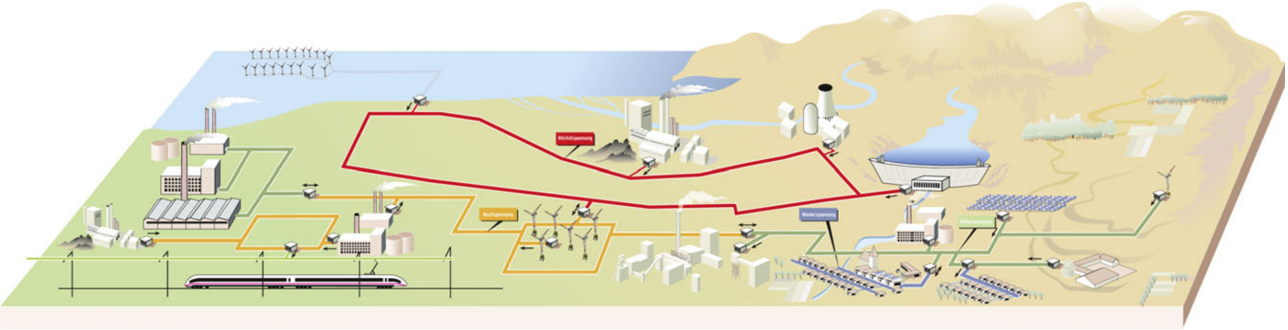


Figure 2. Functions and structures of the various power levels in the power network [7]. © F.A.Z.-Grafik/Karl-Heinz Döring. Wired landscape: Large-scale power plants feed the maximum-voltage transmission network (red), medium-sized power generators feed the high-voltage grid (orange), and smaller municipal power plants feed the medium-voltage grid (green). From there the electricity flows into the low-voltage lines (blue), which end in our home outlets. Through the substations between networks, the energy can principally flow in either direction (double arrows). The railway operates a separate high-voltage grid. It is powered by its own power plants or at least its own generators in other power plants.

seasonal due to consumption by the heating market. The storage locations are shown in Fig. 3.

Function of storage: Worldwide, Germany has the fourth largest natural gas storage facilities, which are also expandable. Gas storage systems compensate the seasonal (pore storage) and daily fluctuations (cavern storage). Supply optimization by taking advantage of fluctuating gas prices also plays an increasing role. Strategic storage is not currently perceived as a political necessity, since the natural gas supply is considered to be secure [8]. Storage systems are therefore operated from a purely commercial point of view. However, at present, strong expansion of storage is taking place with the prospect of developing Germany into a hub for the European gas market.

Notes: The gas grid itself, as a transport network of a chemical energy carrier, can provide both transport and storage functions. The storage capacity of the pipelines is considerable and can compensate for short-term fluctuations without having to exploit actual storage (Fig. 4).

Favored supply of critical power plants for the reliable supply of electricity is not ensured. The natural gas storage facilities are currently operated commercially in compliance with legal regulations. Political problems leading to disruptions of supply may require exports to neighboring European countries.

2.6.3 District and Local Heating, Steam Grids

Grid structure: Local.

Grid function: Secure supply of process heat or space heating to consumers (Fig. 5).

Storage technologies: Grid capacity, thermal storage.

Function of storage: Stability of the heat supply in municipal or industrial sites, decoupling of the operating modes of combined heat and power (CHP) plants, balance of seasonal fluctuations.

Notes: Heating grids can provide both transport and storage functions. However, the storage capacity of the network itself is dependent on the losses that occur, e.g., by incomplete insulation. It can therefore only be used for short-term storage. The amount of heat supplied depends on the consumption. It is possible to take up energy from the power grid via resistance heating. Strong cross-linking of electricity and heat grids exists, e.g., in Denmark. The combination of industrial sites and local district heating networks is often already a reality. The grid load is subject to seasonal fluctuations.

2.6.4 Fuel Grids

Grid structure: EU, national (CEPS and NEPS, operator: FBG)

Grid function: Ensuring strategic supply of major civil and military consumers (airports, ports, refineries) with fuels.

Storage technologies: Fuel storage, grid capacity. Petroleum storage facilities in Germany have a capacity of approximately 27.6 million m^3, which guarantees a supply for around two months. The stockpiling of petroleum products is regulated by law. The law calls for stocking of the respective petroleum products based on the average net imports [9] for 90 days by the *Erdölbevorratungsverband* (Petroleum Stockpiling Agency), which can be done either in Germany or in other countries of the EU. At present, this requirement is met with a reserve of 23.4 million t of crude oil and petroleum products [10]. A strategic Federal reserve for crude oil no longer exists. By decision of the Federal Government, it was dissolved from 1997 to 2001. The storage facilities in Germany are shown in Fig. 4. An example of the military infrastructure is the CEPS (Central European Pipeline System) with more than 5500 km of pipelines, which connects 30 NATO depots and six civilian depots, as well as military and civilian bulk consumers. The system has a total storage capacity of 1.22 million m^3 and is shown in Fig. 6 [12].

Function of storage: Strategic security, civil/military transport infrastructure.

Notes: The fuel grid itself, as a transport network of material energy carriers, can provide both transport and storage functions. The storage capacity of the pipelines and transport containers (tank trucks, tank wagons, filling stations, etc.) is considerable and can compensate for short-term fluctuations, without having to exploit the actual storage.

The fuel supply of other consumers is ensured via a logistical infrastructure distributing the fuel, starting from the major ports with large storage facilities (e.g., Hamburg, Rotterdam), by barge, rail transport, and trucks. At the nodes and distribution centers, fuels are stored above ground in large tanks.

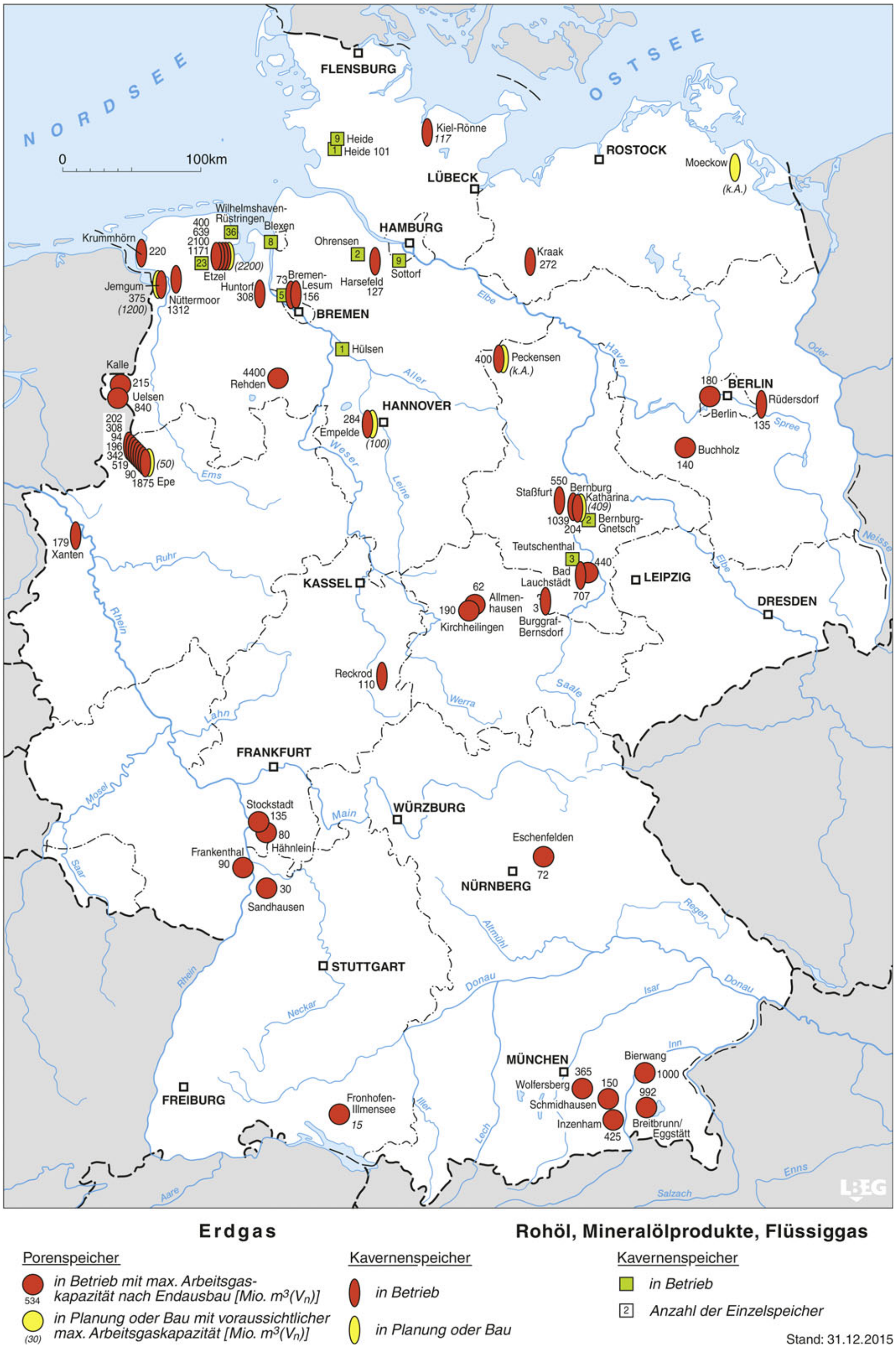


Figure 3. Storage locations for natural gas, crude oil products, and liquefied gas in Germany; © State Office for Mining, Energy and Geology [10]. Natural gas is stored in pore storage (circles) which are marked as operational (red) or planed (yellow) with their respective capacity in Mio. m^3(Vn); natural gas cavern storage is marked by elliptical symbols with the same color coding; cavern storage for mineral oil, oil-based products and liquefied natural gas are marked by green square symbols; the number indicates the number of individual caverns.

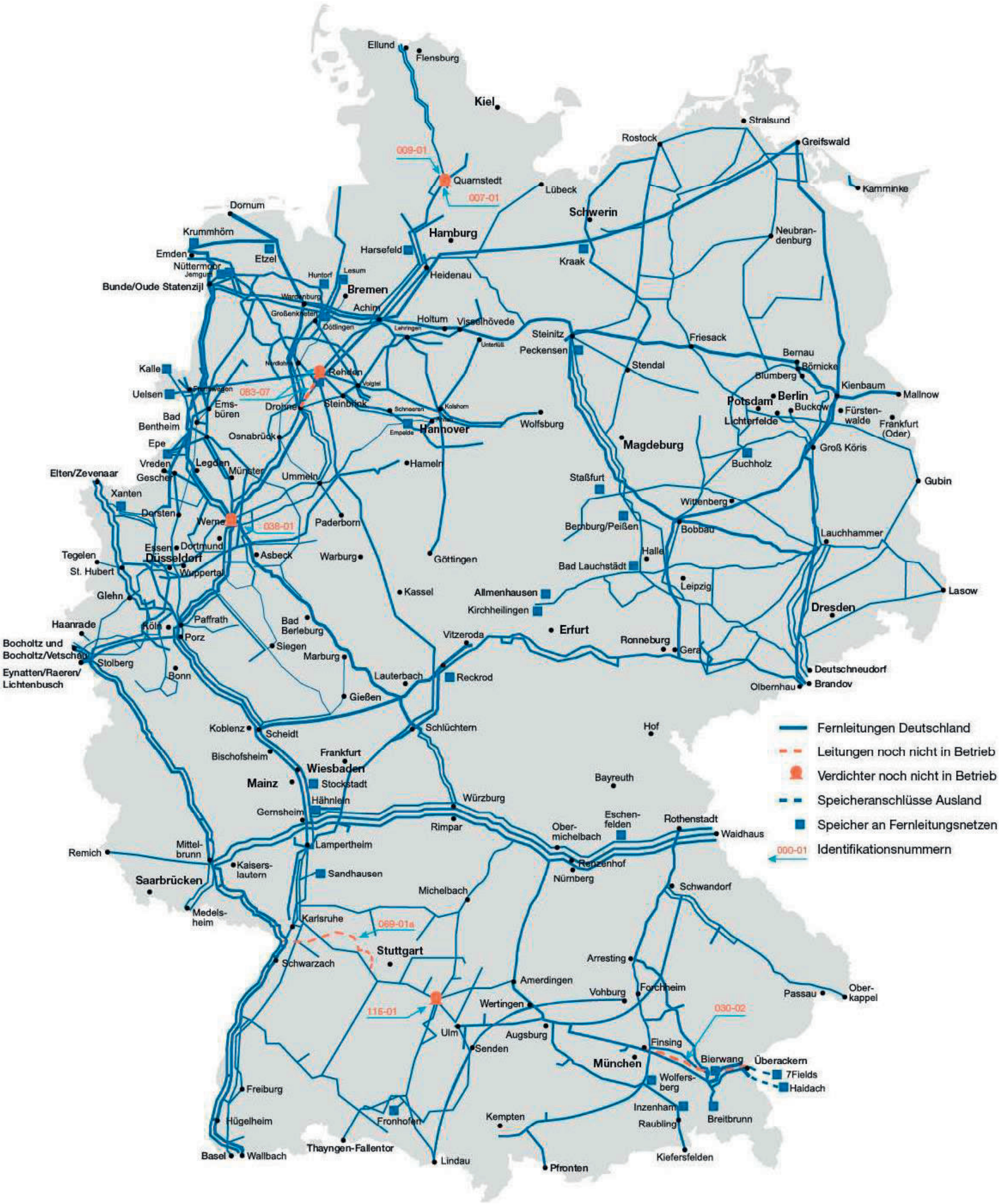


Figure 4. Overview of the German gas pipeline network at a glance; © TSOs [11]. Solid blue lines: existing transmission pipelines; dashed orange lines: existing pipelines; orange symbols: gas compression stations for which operation has not started yet; dashed blue lines: connections gas storage in neighboring countries; solid blue squares: domestic gas storage facilities.

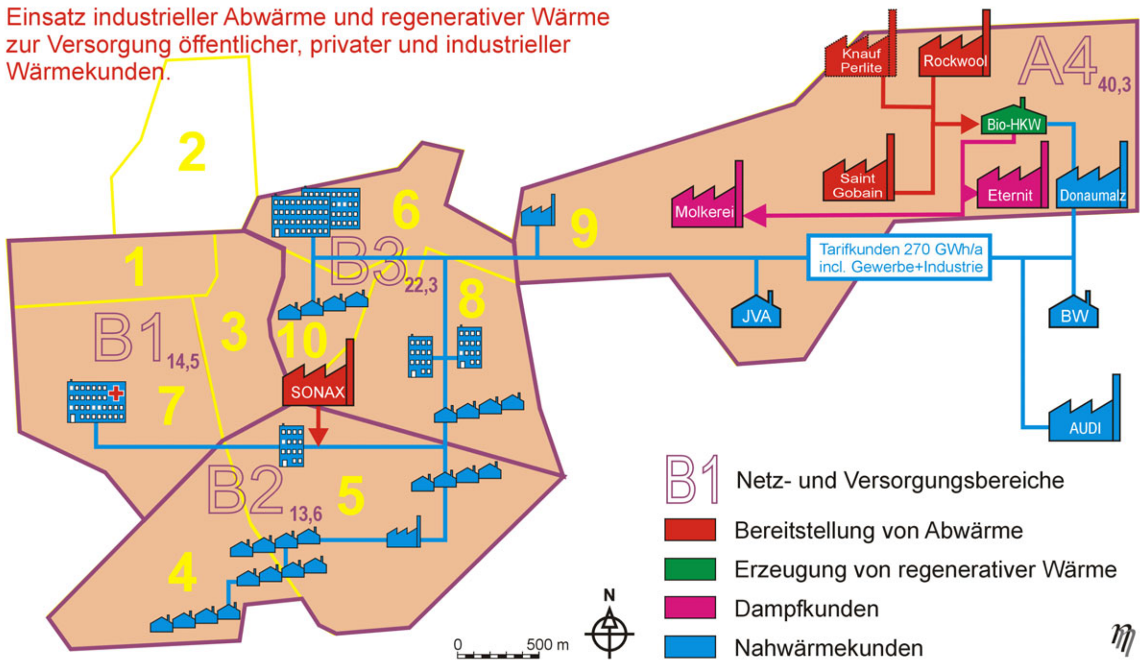


Figure 5. Structure of the combined local and district heating networks of Neuburg on the Donau to integrate industrial waste heat in municipal district heating; © eta energy consulting GbR [13]. Utilization of industrial waste heat and renewable heat to supply public, private and industrial customers (total amount of required heat: 270 $\mathrm{GWh_{th}a^{-1}}$); letters and numbers: supply regions; red symbols: industrial waste heat sources; green symbols: renewable heat sources; magenta symbols: customers requiring steam; blue symbols: district heating customers.

2.6.5 Summary of the Current Status of Storage and Grids

Currently, the different energy supply and distribution grids are operated independently. Stronger coupling of the energy networks raises the question of a common communication and regulation structure for the necessary mutual coordination.

An overview of the grids and storage facilities is given in Tab. 2. It shows that the gas and fuel grids have large storage facilities, whereas capacities for storing electricity and heat are insufficient. The technical difficulty is the low storage density of electricity- and heat-storage systems, each of which requires a storage medium. In contrast, as chemical storage systems, the energy resources fuel and natural gas have high energy densities.

Table 2. Network-attached storage; projects under construction/planned in parentheses [10].

Grid	Storage type	Amount	Capacity	Power	Discharge time	Notes
Electricity	Pumped-storage hydroelectric power plants	35 (+14)	40 (+>13) GWh	7 (+6) GW	6 h	Annual energy demand ca. 600 TWh; pumped storage covers ca. 35 min. of this requirement.
	Diabatic compressed air energy storage	1	600 MWh	321 MW	2 h	
Natural gas	Pore storage	20 locations	9784 million m^3 (working gas volume)	7 085 000 m^3h^{-1}	58 d	
	Cavern storage	30 locations, 260 storage sites	14 315 million m^3 (working gas volume)	20 167 000 m^3h^{-1}	30 d	
Heat	No major storage					
Oil	Cavern storage for crude oil, petroleum products, and liquefied petroleum gas	103 (12 locations)	27 601 (+3800) (million m^3)			Covers total demand of oil for about 59 d.

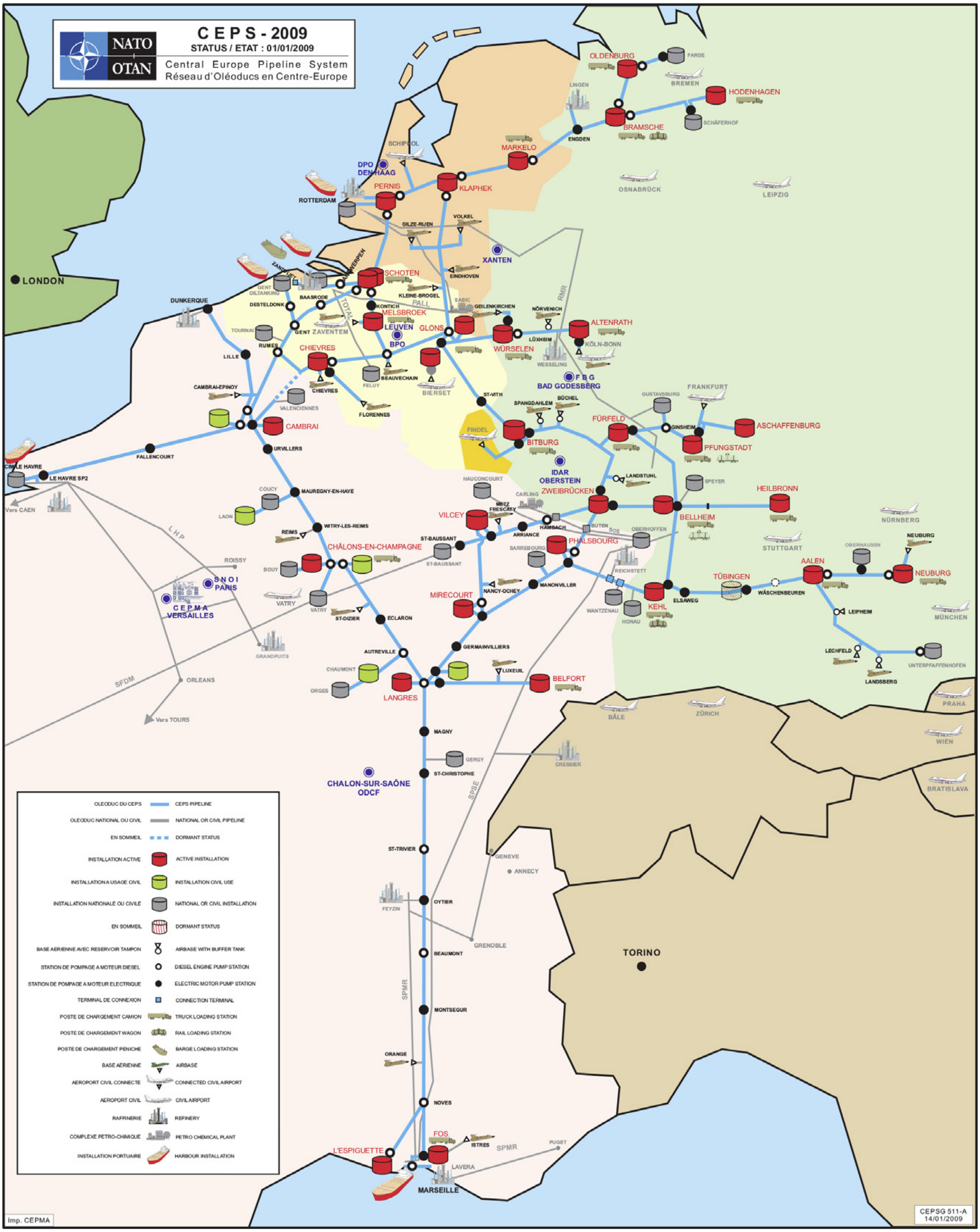


Figure 6. Map of the NATO pipeline network CEPS; © NATO [12].

3 Evaluation Criteria and Scenarios for the Integrated Use of Energy Storage Technologies

Energy storage can be based on different technologies and serve the most diverse requirements. Some energy storage technologies are summarized in Tab. 3, and their diversity already clearly indicates the complexity of the subject "energy storage".

3.1 Tasks and Functions of Energy Storage

For a secure and efficient energy supply, supply and consumption must be in temporal and spatial balance. This task is performed mainly by the grids; if necessary, the energy supply is adjusted. The situation is critical above all for the electric power grid, since it has no inherent capacity to compensate for imbalances that affect the grid frequency. The example of the electricity supply can be taken to illustrate the functions, advantages, and limitations of energy storage systems.

3.1.1 Definition: Residual Load

In this article, the term "residual load" refers to the difference between the load (demand) and production (supply) and has the units of power (e.g., kW). A positive residual load means that demand exceeds supply (additional power plants must be used), while a negative residual load indicates excess production (power stations must be switched off).

3.1.2 Definition: Load-Duration Curve

The load-duration curve describes the residual load over a selected period of time (e.g., a year). The values of the residual load are not presented chronologically, but sorted in descending order (see the figures in the next section). The conclusion would then be: e.g., in the year under consideration (8760 h), there were 2000 h with a positive residual load, that is, more demand than supply, 5000 h with a balanced load, and 1760 h with an excess supply of energy.

3.1.3 Smoothing of Random Fluctuations

The random behavior of consumers cannot be fully predicted. Therefore, this automatically leads to fluctuations, the so-called load forecast error, of the readily predictable mean value of the residual load, which can be described as a normal distribution and must be balanced [14]. In the case of normally distributed fluctuations, a significant attenuation of the peaks can already be achieved with a relatively small rechargeable storage unit. A prerequisite is that charging and discharging of the storage are fast with respect to the fluctuations. This is illustrated in Fig. 7. The storage unit can both emit energy (dark rectangle) and thus reduce a positive residual load (load surplus) as well as absorb energy (light rectangle) and thus reduce a negative residual load (production surplus). The height of the rectangles represents the performance of the storage unit, and the area is equal to the capacity. The load-duration curves sort the load curves according to their absolute values. In the case of a normal distribution around a mean value, the variation curves are symmetrical. The effect of energy storage, which compensates 80 % of the variation, is reflected mainly in the central regions of the load-duration curve, where deviations are compensated. Storage cannot counterbalance the fluctuations if they exceed its power consumption and dissipation. If the capacity of the energy storage system allows no further energy uptake or release, then positive or negative fluctuations cannot be subdued until the storage has had the opportunity to be either discharged or charged.

Table 3. Examples of energy storage.

Storage technology	Form of energy loading	Form of energy discharge	Storage of energy as
Hydroelectric pumped storage	Electricity	Electricity	Potential energy (height difference)
Battery	Electricity	Electricity	Electrochemical potential (charge separation)
Flywheel storage	Electricity	Electricity	Kinetic energy (velocity difference)
Warm-water storage	Heat	Heat	Sensible heat (temperature difference)
Compressed-air reservoir	Electricity	Electricity	Inner energy (pressure difference)
Phase-change materials	Heat	Heat	Latent heat (phase transition enthalpy)
Thermochemical storage	Heat	Heat	Chemical bond (enthalpy)
Power-to-gas/liquid/X (hydrogen, methane, methanol, etc.)	Electricity	Heat and possibly electricity or mechanical energy	Chemical bond (enthalpy)
Fossil fuels: coal, oil, natural gas	Solar energy	Heat and possibly electricity and mechanical energy	Chemical bond (enthalpy)
Biomass	Solar energy	Heat and possibly electricity	Chemical bond (enthalpy)
Biodiesel	Solar energy	Heat and mechanical energy	Chemical bond (enthalpy)

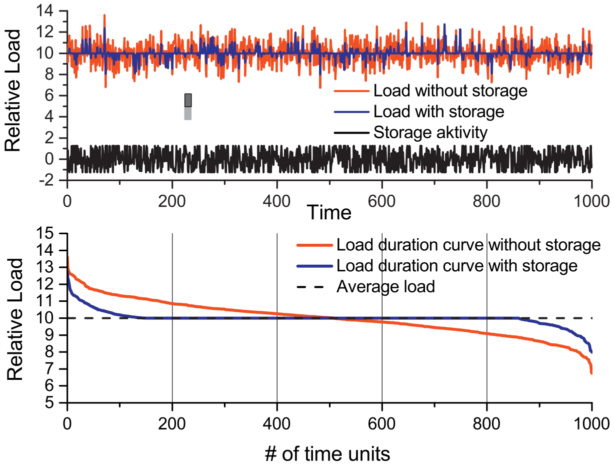


Figure 7. Impact of storage on the smoothing of the residual load. The residual load fluctuates statistically with a normal distribution (standard deviation: 10 %) around the mean.

The design of the energy storage system depends on the desired smoothing of the curve and must be economically optimized, especially with regard to smart combination with other means to smooth the residual load (e.g., import/export of energy).

3.1.4 Compensating a Systematically Higher Supply

If the supply of a grid is continuously higher than the demand, compensation can no longer be carried out exclusively in the framework of the considered grid. The available excess energy supply must then either be reduced, e.g., by shutting down power plants, or the excess energy is converted to another form of energy that is either consumed or stored.

A storage technology can only meet this requirement if it removes the excess energy from the original grid permanently by transforming it into another form of energy, which may also be more readily stored. This is illustrated in Fig. 8. The effect on the residual load is made clear by the smoothing in the form of the gray line in relation to the original residual load. The area of the rectangle represents the total energy that is received by the storage system. The height of the rectangle corresponds to the maximum power consumption of the storage system. In this example, the average excess of the residual load is identical to the maximum power consumption of the storage system. The average power consumption is equivalent to 75 % of the maximum. The fluctuations of power and load are normally distributed around the average values with a standard deviation equal to half of the average excess. The load-duration curves clearly show the effect of the additional decrease in performance. The reduction is carried out exclusively asymmetrically in the central region of the positive residual load.

For the subsequent use of this stored excess energy, the options of the new energy forms are available, such as coupling to another energy grid and material use if a storage material can be used as a raw material.

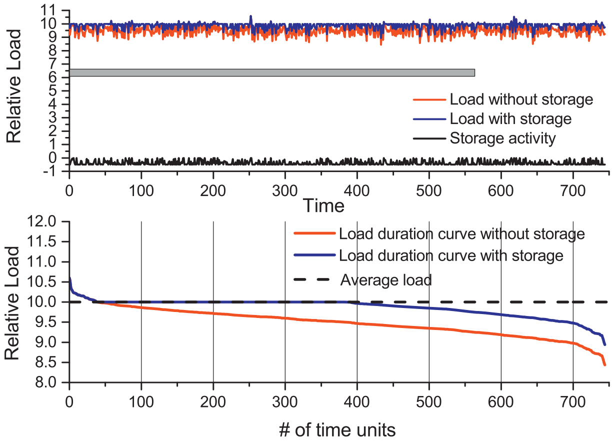


Figure 8. Effect of an additional load decrease on systematic oversupply.

Storage technologies for this function will in general be a combination of individual solutions. For example, power-to-gas concepts would convert the excess electricity to hydrogen by electrolysis of water. This hydrogen could power a gas turbine to generate electricity, albeit with low efficiency, be used for mobility in fuel-cell cars, or, after conversion with carbon dioxide to methane, be fed into the natural gas grid, or be stored in the form of liquid fuels. Alternatively, the hydrogen could also be used in metallurgical, chemical, or petrochemical processes.

This example illustrates how different technology chains can fulfill the function of energy storage and how coupling with other forms of energy opens up new degrees of freedom in the use of energy that were not accessible to the original form of energy.

3.1.5 Compensating a Systematically Higher Demand

Similar to the above case, it is also impossible to achieve a balance between supply and demand solely in the energy system under consideration if demand is consistently higher than the corresponding supply. In this case, the needed additional energy must be supplied from outside the system. This can be done, e.g., through the supply of additional power plant capacity for the electrical grid.

Another contribution may be provided by storage technology that feeds the energy of an independent system with higher supply than demand, optionally after a transformation process, into the system under consideration. This is analogous to the case considered above and illustrated in Fig. 9. The effect is illustrated by the smoothing in the form of the gray line in relation to the original residual load. The area of the rectangle represents the total energy that is output from the storage system, and the height of the rectangle corresponds to its maximum power output. In this example, the mean deficit of the residual load is identical to the maximum power output of the storage unit. The average power output is equivalent to 75 % of the maximum. The fluctuations of power and load are normally distributed with a standard deviation equal to half the average

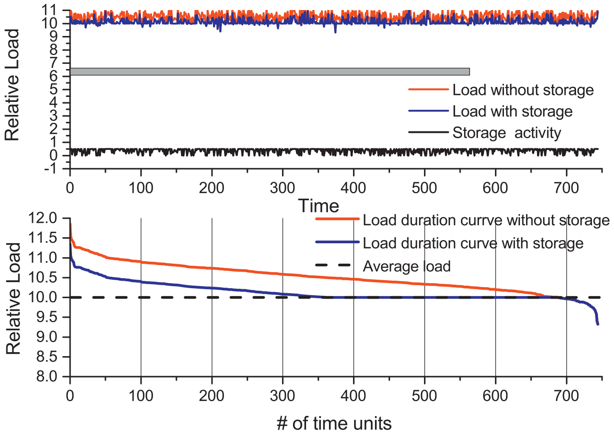


Figure 9. Effect of an additional load supply on systematic undersupply.

excess about the mean values. A combination of the two energy systems into a whole system may, under certain circumstances, be an attractive alternative in terms of efficient use of energy. Whether this option is also cost-effective, must be checked on a case-by-case basis.

3.1.6 Structured Fluctuations

Structured fluctuations can be regarded as combinations of different supply/demand situations that can be compensated within an observed time interval. As shown in Fig. 10, it is not primarily about smoothing of the profile, but about the postponement of the resulting surplus energy for supply in times of inadequate load coverage. The total storage capacity is given by the larger of the two areas: either the sum of the light gray rectangles (power output) or the dark gray rectangle (power) defines the required capacity. The requirements for power consumption and dissipation are different. On the load-duration curve it is clearly evident that a surplus occurs only during daylight hours.

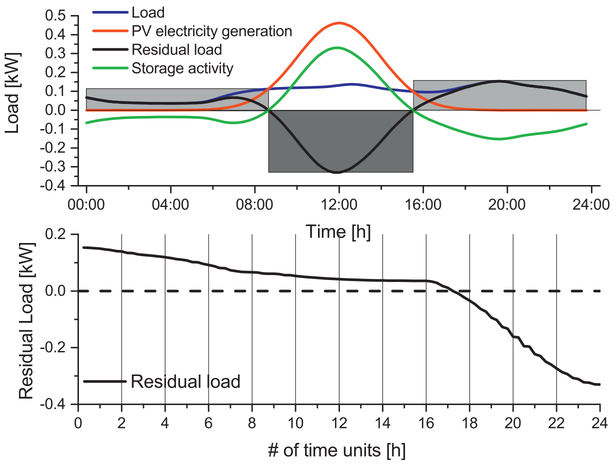


Figure 10. Schematic representation of a storage system to compensate for structured variation; example of a daily load curve of a photovoltaic system and the electricity demand.

Therefore, the storage capacity must be high enough that load coverage is secured during the entire period. It is also noteworthy that the requirements for power uptake and release are usually not identical. An example is a hot-water tank for radiators, which is charged quickly, whereas the heat is emitted over a longer period with lower power.

The power uptake is defined by the difference between the maximum power and the load, while the power output in this example is given by the daily course of the electricity demand. In comparison to the smoothing of random fluctuations, the storage capacity is much greater due to the time-structured energy production, but the number of cycles is lower.

Thus, storage systems whose investment costs are significantly defined by their capacity (e.g., batteries) in this case are generally not economically favored. The different requirements for power uptake, power output, and capacity suggest that this storage function should not be met by a single storage unit, but by an integrated system of individual elements that can cover the various requirements separately through optimal technical solutions.

3.1.7 Energy Storage Systems: Requirements and Functions

The demands on energy storage systems vary greatly depending on the purpose for which they are used. In contrast to the above idealized cases, the balance between supply and demand in a real energy system can be regarded as a combination of these ideal cases, each of which makes different contributions. In Tab. 4, the individual cases and their respective requirements are summarized.

3.2 Energetic Potential Analysis

3.2.1 Fundamental Considerations for Energy Conversion

The storage of energy in the same form is often neither possible nor advantageous. However, transformation to another form of energy is always associated with losses. As part of the process chain starting from the use of the primary energy carrier, through storage, to the use of the desired energy form, each step can be assigned an efficiency value. In real systems this efficiency is always < 1. The overall efficiency of the entire sequential process chain corresponds to the product of the efficiencies of the individual process steps. This results in the following three prerequisites for energetically efficient use of the process chain:

- Minimizing the number of process steps from the primary energy carrier to the consumer.
- Carrying out the individual process steps in the process chain with the highest possible efficiency.
- Minimizing the number of conversions between various forms of energy and energy carriers, since they are relatively inefficient.

Table 4. Overview of the different storage functions and their requirements.

Storage task	Storage function	Requirements power	Requirements capacity	Technology examples
Random fluctuations in the residual load profile around the mean	Smoothing of the residual load profile	Relatively (equal) high power and release	Low capacity	Pumped-storage power plants, batteries, flywheel, sensible thermal storage
Systematic surplus	Providing additional load	Adequate power input	Mostly unlimited capacity	Electrolysis
Systematic deficit	Providing additional power	Adequate power output	Mostly unlimited capacity	Power plants
Structured fluctuations	Postponement of the power provided (load levelling)	Differently dimensioned power consumption and release	High capacity	Redox flow batteries, phase-change materials

3.2.2 Properties of Storage Technologies

Capacity

The capacity of a storage unit (expressed in units of energy, e.g., Wh, J, TCE, TOE, etc.) indicates how much energy the storage medium can take up. It is defined by the energy density of the storage medium and its energy form. The mass-normalized storage density of heat and electricity storage is generally rather low, whereas that of chemical storage is relatively high. Thus, electrical energy is stored in, e.g., batteries by electrochemical charge separation, the extent of which depends on the particular combination of materials and their quantities.

In addition to the mass-normalized storage density, depending on the application, the volume-normalized storage density may also play a central role. Solids and liquids (e.g., gasoline and coal) have a higher storage density than gases (e.g., hydrogen and methane), which must be compressed to obtain acceptable volumetric energy densities.

In general, the application profile of a storage technology determines the demands on the capacity. Storage for mobile applications should be small, light, and compact, with a clearly defined, limited capacity (e.g., a fuel tank). In contrast, a stationary power-to-gas plant for the production of hydrogen would have a virtually freely scalable capacity that would be limited only by the size of the connected storage cavern or the amount of gas that can be fed into the gas grid.

Power Input/Output

An important performance indicator of a storage system is the amount of energy absorbed or released by the system per unit time (expressed in terms of energy per unit time, e.g., W). Depending on the application, the requirements for power uptake and discharge may be different. Pumped-storage hydroelectric plants, which inter alia are intended to offset the random fluctuations in the power grid, are designed such that power uptake and release are of similar magnitude. In contrast, the power consumption of seasonal heat storage devices is relatively high compared to their power output. The storage unit is loaded relatively quickly, whereas discharge is extended over a longer period of time.

Moreover, power absorption and release may involve different forms of energy. In the above example of a heat accumulator, charging can be done electrically, while discharge occurs as thermal energy by means of a heat carrier (e.g., hot water or steam). It is therefore essential to clearly define the performance requirements of the storage system related to the purposes of the application in order to select the appropriate system.

Full-Load Cycle Number

The full-load cycle number (expressed as frequency in units of reciprocal time, e.g., h^{-1}) is a calculated parameter (similar to the full-load hours of a power plant) which describes how often a storage system has been fully charged and discharged per unit time. Partial charging and discharging are added up. Conclusion about the time-resolved storage demand cannot be made on the basis of the full-load cycle number. It is limited by the materials used and defined by the desired application. In principle, the highest possible full-load cycle number is desirable for economic operation of energy storage systems.

Some applications, such as the compensation of random fluctuations, lead to frequent stress on the storage system, and thus to a high full-load cycle number at a low storage capacity, while a seasonal heat storage is charged and discharged only once a year. The full-load cycle number is a property of the overall system. Thus, in a power-to-gas system, a cycle is only completed when the produced gas is used.

Especially electrochemical storage technologies are characterized not only by the calendar life, but also by the cycle life. Charging and discharging cycles lead to irreversible changes in the material structure that, after a certain number of cycles, will make it unusable for further use as a storage material. Unlike electrochemical systems, the cycle life of mechanical storage is practically unlimited, provided the appropriate maintenance and the replacement of defective parts is performed.

Efficiency

The efficiency of a process can be expressed as a percentage or as a fraction. It is the ratio of the energy output to the input. The efficiency itself is generally based on a particular product or a particular form of energy. It defines, e.g., how much of the energy used is incorporated in the product or how much electrical energy can be generated in a power plant by a combustion process in comparison to the chemical energy of the fuel itself. The efficiency of a storage system indicates the amount of energy that is available for discharge relative to the amount stored.

The theoretical efficiency, e.g., of a chemical reaction, is always greater than that achieved in its technical implementation, since additional losses occur. For technical processes the validity of a specified efficiency is severely limited unless other operating parameters are clearly specified. Frequently, it is implicitly assumed that the process is operated at its optimum operating point. The implementation of a process often includes peripheral processes, e.g. gas purification, which also increase the cost, and thus reduce the overall system efficiency. If it is not stated whether the energy requirements of the peripheral processes have been included, specification of the efficiency is often not very meaningful.

Assessment of different efficiencies and their comparison with one other is therefore only possible if the exact conditions of the efficiencies are known. Since this is not guaranteed for all sources in this document, the efficiencies given here should rather be considered in terms of orders of magnitude and not as exact values.

The overall efficiency of a sequential process chain is given by the product of the efficiencies of the individual process steps, whereby the efficiency definitions must be compatible with each other. Since there are always energy losses in power conversion, the efficiency of a process chain is always less than 100 %.

For a more detailed discussion, the reader is referred to the example of the efficiency definition for an electrolyzer used for the electrolysis of water [15], in which its meaningfulness and its limits are discussed.

In the following sections, the following efficiency definitions are used:

- The electrical efficiency refers to the amount of electricity supplied compared to the input amount (e.g., battery storage).
- Efficiency (LHV, lower heating value) refers to the efficiency of a combustion or conversion process based on the net calorific value, whereby the heat of condensation of the water vapor cannot be used (e.g., fuels).
- Efficiency (HHV, higher heating value) refers to the efficiency of a combustion or conversion process on the basis of the gross calorific value, whereby the heat of condensation of water vapor can be used (e.g., chemical processes).

Response Time

The power uptake and release of the selected storage technology must be sufficiently fast to respond to the variability of the application under consideration. Fluctuations in the power grid, e.g., caused by fluctuating feed of wind energy, can be compensated quickly enough through the use of batteries, whereas sensible-heat storage would react too slowly to generate steam with a connected turbine. If the storage function is performed by process chains, usually the slowest step determines the response time (expressed in units of time, e.g., s) of the entire chain.

3.3 Economic Evaluation

3.3.1 Fundamentals of the Cost-Effectiveness of Storage Technologies

The main focus of this position paper lies on the scientific and technological feasibility rather than an economic analysis. The scientific and technological feasibility is a necessary but not sufficient prerequisite for the use of storage technology. The decision to implement a particular storage technology should be made only after a thorough economic and business evaluation. This will always be done on a case-by-case basis. However, there are some aspects of a more general nature.

3.3.2 Grid Services

Storage technologies can contribute to the stability of the supply grid through an improved balance between supply and demand and facilitate more flexibility. By providing additional balancing power, they allow a decrease in reserve capacity, reduce the required grid expansion, and help to eliminate bottlenecks. They can increase the service quality of the entire grid and thus provide an universal grid service, regardless of the specific degree of utilization of individual storage units, from which all system users benefit.

The power grid is a special case, since a technical possibility for long-term storage of electricity once it is generated does not exist at present. Short-term storage is possible, but is not specifically remunerated as a grid service.

The traditional business model of pumped-storage hydroelectric power stations is based on the utilization of the price difference between periods of high and low consumption (the so-called spread). Currently, this model offers only limited economic viability, because the original high-price periods (afternoons) are now covered by a relatively high contribution of photovoltaics, which have feed-in priority independent of the electricity price.

For the supply of electrical energy, the operators of pumped-storage hydroelectric power stations, but also industrial companies with flexible processes, usually negotiate contracts with grid operators. A list of companies that offer reserve-energy capacity is available on the internet [16]. It is apparent that the main suppliers of reserve-energy capacity themselves belong to the energy sector, supplemented by public utilities and site operators. Individual industrial providers are mainly active in the metals and chemicals sector. Geographically, not all suppliers are located in Germany, but also in neighboring Alpine countries, which clearly highlights the European dimension of power grids.

Conversely, improved grid stability tends to lead to a lower utilization of storage units, which affects their profitability. It is therefore to be expected that a too massive expansion of storage technology is not necessarily the most economic method for grid stabilization and decreases the economic conditions of the individual storage units.

3.3.3 Storage Usage

In the best-case scenario, a storage unit is charged and discharged as completely as possible with high frequency. In general, the more frequently a storage unit is used, the more likely it can be operated economically. This, however, strongly depends on the particular application. The faster a storage technology is capable of reacting to the grid, the more likely it can exploit short-term price fluctuations and the greater its potential contribution to grid stability.

3.3.4 Investment Costs

The investment costs are written off over the amortization period, or the total number of cycles and the utilization of the storage. Depending on storage technology, they vary greatly. Investments with long amortization periods presuppose a confidence in the appropriate political and economic framework. The technical lifetime is usually longer and ranges from a few years (batteries) up to 100 years (pumped storage).

3.3.5 Operating Costs

In general, the energy that is fed into a storage unit is not free. The universal business model for storage technologies utilizes the difference in the market price of the energy output and input.

In exceptional cases, electrical energy is traded at negative prices at the electricity exchange. This excess electricity is currently still very manageable. It is generally expected that the amount of excess electricity will increase with the expansion of volatile renewable energies, that is, wind and photovoltaics [17]. However, negative electricity prices cannot increase without limit since at a certain price, it will be more favorable for the producer to switch off the plant than pay for supplying the surplus electricity. Acceptance fees are currently guaranteed under the EEG remuneration for renewable energy, and therefore the maximum value of the negative electricity price is set before a down-regulation of the corresponding assets becomes more favorable. The current version of the EEG (Sect. 51), restricts the remuneration in times of negative electricity prices [18].

As a measure of the excess amount of electricity, the amount of dumped energy from EEG electricity can be used. In 2015, 4.7 TWh was dumped from renewable sources [19]. For 2024, an amount of dumped energy on the order of 0 – 8.8 TWh (0 – 2.5 % of the predicted renewable electricity generation) is expected [17]. However, this amount of dumped energy is manageable. A dena study estimated, depending on the scenario, from 2.5 to 12 TWh of "non-integrable energy" by 2030 [20]. In comparison, the current trade balance, i.e., the net amount of current exports by Germany to neighboring countries, amounted to 51.8 TWh in 2015 [21].

In this case as well, a strong expansion of storage technologies would in principle stabilize prices by increased demand and reduce the surplus quantities of electricity. An uncontrolled expansion of storage technologies would lead its own business model ad absurdum.

This business model is obviously not suitable for long-term storage, and consequently, stockpiling of strategic reserves of natural gas and oil is regulated by law.

This reveals a fundamental dilemma. From an economic perspective, storage technologies serve to smooth the difference between the load and generation and, therefore, to smooth out the price differences. From a business perspective, precisely these differences between charging and discharging and the associated price differences constitute the basis for economic operation of the storage system.

3.3.6 Process Chains

The function of energy storage does not need to be met by a single storage technology and can be provided as a process chain of various technologies. A process chain can be significantly better adapted to specific storage requirements and especially to their changes. It also allows cross-links to other areas of the energy system to be established and thus increases the flexibility of the overall system. However, the downstream process steps must also be considered for a full economic analysis.

3.3.7 Alternative Uses of Chemical Storage

In virtually all cases, there are alternative uses of substances produced for energy storage. Markets exist in which pricing of these substances is performed. For example, methanol is a basic chemical product that is traded and has a global market price. Since, in principle, the same potential applications exist for the storage substance as for the original substance produced for other purposes, they are in direct economic competition with each other. Its use as a storage substance is in competition with conventional industrial value chains. However, in addition, the relative dimensions for use in energy applications and the alternative uses must be taken into consideration.

A final evaluation of the efficiency of a storage system is always dependent on the selected reference case and the associated conditions. For example, the VDE study “Energy Storage in Power Supply Systems with a High Proportion of Renewable Energy Sources” [22] compiles the full costs of the storage systems under certain operating scenarios. In Sect. 5, simplified cost assessments are carried out for different reference cases.

4 Storage Technologies

4.1 Technologies for Storage as Mechanical Energy

Mechanical storage systems form the basis of the storage reserve in the power supply. The most mature technology is used in pumped-storage hydroelectric power stations, which can provide both positive and negative balancing power. Currently, pumped-storage hydroelectric power stations are the only available large-scale storage technology for electricity. They need certain geographical conditions and their relatively low energy density leads to large storage volumes. The development potential is relatively limited due to geographical requirements and, above all, the lack of acceptance within the population in Germany.

For the use of compressed-air energy storage a wealth of experience is already available. By combination with thermal storage, it can be operated adiabatically, which is reflected in a significantly higher degree of efficiency, but also in higher investment costs. For a further expansion of compressed-air energy storage technology, possible competition with the use of caverns for the storage of natural gas or hydrogen must be taken into consideration. However, this competition is limited to caverns of lower depths. Hydrogen and natural gas are usually stored at high pressures, which require depths of about 1000 m. This is much deeper than the depth required for compressed air. Flywheel storage has so far only been used in industrial applications. Flywheels provide high power output but have only a small capacity. The different technologies are compared in Tab. 5.

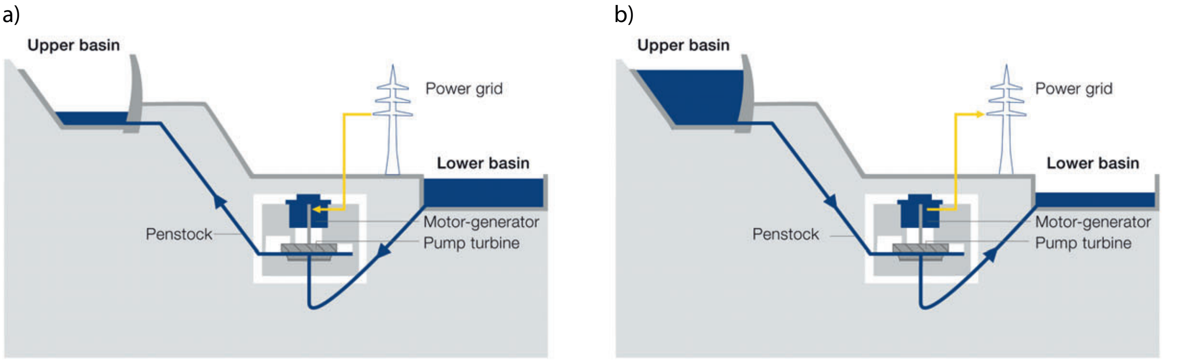
4.1.1 Pumped-Storage Hydroelectric Power Stations

Pumped-storage hydroelectric power stations have been used on an industrial scale for more than 80 years. They are linked to specific geographical conditions. Energy is stored in the form of the potential energy due to the difference in height of the upper and lower reservoirs and the mass of the storage medium water. If the grid has more power than can be used, water is pumped from the lower reservoir to the upper reservoir. During times of increased demand for electricity, water flows from the upper reservoir through a turbine into the lower reservoir, generating electricity which is fed into the grid (Fig. 11).

Table 5. Storage in the form of mechanical energy [2, 22–24]. The figures serve as benchmarks.

Technology	Pumped-storage hydroelectric power plant	Pumped-storage hydroelectric power plant, mine	Compressed-air storage, diabatic	Compressed-air storage, adiabatic	Flywheel	Air liquefaction
Performance range	MW–GW	MW–GW	MW–GW	MW–GW	10 kW–20 MW	10–250 MW
Capacity	MWh–GWh	MWh–GWh	MWh–GWh	MWh–GWh	kWh	MWh–GWh
Reaction time	min	min	15 min	15 min	s	20 min
Maximum number of cycles	20 000		30 000	30 000	1 000 000	
Plant life [a][a]	50–100		< 50	< 50	20	> 30
Cycle efficiency[b] (electrical) [%]	≤ 80		42 (Huntdorf, D); 54 (McIntosh, USA)	70	85–90	50–60
Specific energy density [$\mathrm{Wh\,kg^{-1}}$]	Depending on height difference, average ca. 0.7	Depending on height difference, average ca. 0.7			< 5	439
Volumetric energy density [$\mathrm{Wh\,L^{-1}}$]	Depending on height difference, average ca. 0.7	Depending on height difference, average ca. 0.7	2–5	2.9	10	
Specific power density [$\mathrm{W\,kg^{-1}}$]					275	
Investment costs, power (system) [€ $\mathrm{kW^{-1}}$]	500–1000	1800	1000	1000	100–360	625–1400
Investment costs, capacity (system) [€ $\mathrm{kWh^{-1}}$]	5–20	25	≥ 40	≈80	1000	
Typical Application	Load leveling, balancing energy, arbitrage	Load leveling, balancing energy, arbitrage	Load leveling, balancing energy, arbitrage	Load leveling, balancing energy, arbitrage	Power quality, control energy	Load leveling, balancing energy, arbitrage
State of technology	Technical implementation	Research	Demonstration	Development	Technical implementation	Development
Notes	Ca. 40 plants (D); power: 7 GW; capacity: 40 GWh		Worldwide: 2 plants; power (D): 321 MW; capacity (D): 642 MWh	Originally planned: 1 plant; power: 90 MW; capacity: 360 MWh	Self-discharge 3–20 % $\mathrm{h^{-1}}$	Air liquefaction as technology is state of the art, use as a storage is in development

[a] Includes sharing of key power plant components; [b] see discussion in Sect. 3.2.



Storage of electricity - pump operation
1. Power is taken from the power grid to run the electric motor.
2. The electric motor drives the pump turbine.
3. The water from the lower basin is pumped into the upper basin.

Generation of electricity - turbine operation
1. The water is fed from the upper basin through a penstock to the pump turbine and drives it.
2. The turbine drives the generator, which produces electricity and releases it into the grid.
3. The water flows into the lower basin.

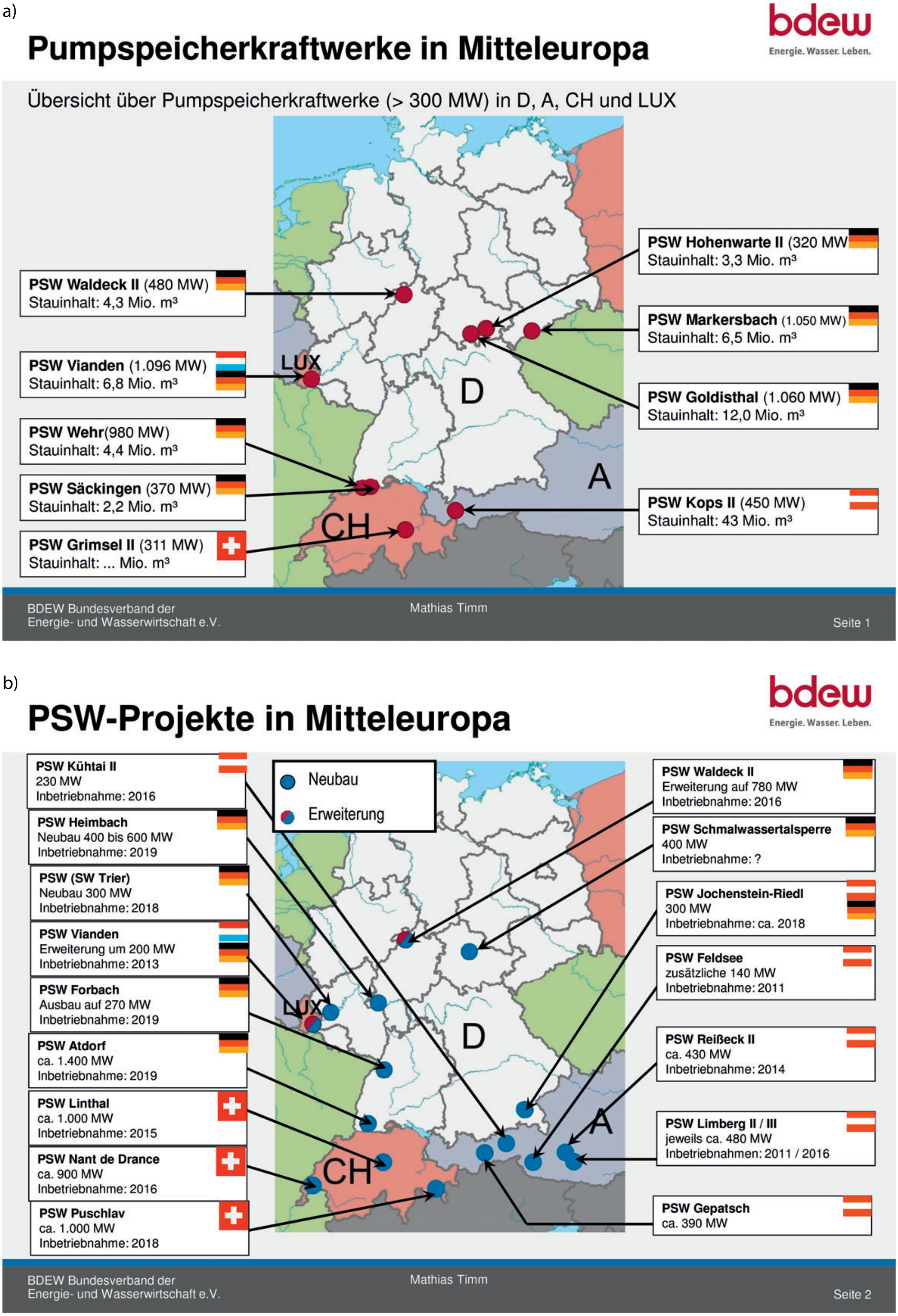
Figure 11. (a, b) Operating principle of a pumped-storage power plant and (c) Raccoon Mountain Pumped Storage Plant at Tennessee River, USA; © Voith GmbH [31].

The technology is very reliable and mature. The electricity-to-power efficiency of a modern pumped-storage hydroelectric power station is approximately 80 % [25]. The disadvantages of pumped-storage power stations lie in the high investment costs, the geographical conditions, and the associated low degree of societal acceptance. Currently, Germany has an output of around 7 GW with a storage capacity of 40 GWh. Geographically, the hydroelectric pumped-storage power plants are mainly located in the southern and central parts of Germany (Fig. 12). A new concept integrates water storage tanks directly into the foundation of a wind mill, in effect a small hydroelectric power station. A pilot unit with an energy storage capacity of 70 MWh is being built in Gaildorf (southern Germany) by Naturspeicher GmbH [26]. Current considerations to take advantage of former mines as underground pumped-storage power stations are still in the research stage [27]. The challenges lie in the development of a cost-effective system concept, whereby in particular the reservoir must be newly created.

4.1.2 Compressed-Air Reservoirs (Diabatic, Adiabatic)

Compressed-air reservoirs use electricity for the compression of air in storage caverns (Fig. 13 a). When electricity is required, the compressed air is decompressed via a gas turbine and thus generates electricity, which is then fed back into the grid. Storage caverns can be, among others, salt caverns, especially in northern Germany. During compression of the air, a significant amount of heat is generated, which is emitted as waste heat into the environment in the case of a diabatically operated reservoir. Conversely, during the expansion of the working gas through a gas turbine additional heat is required since the gas is strongly cooled. In a diabatic compressed-air reservoir, this heat is supplied by means of gas burners. Ultimately, the heat losses and the necessary heat input limit the (electricity-to-electricity) efficiency of diabatically operated compressed-air storage to about 50 %.

Worldwide, only two diabatic compressed-air energy reservoirs are in use. The compressed-air reservoir in Huntorf (Fig. 13 b) has been in operation since 1978, with an output of



a)

Pumpspeicherkraftwerke in Mitteleuropa

bdew
Energie. Wasser. Leben.

Übersicht über Pumpspeicherkraftwerke (> 300 MW) in D, A, CH und LUX

PSW Waldeck II (480 MW)
Stauinhalt: 4,3 Mio. m³

PSW Vianden (1.096 MW)
Stauinhalt: 6,8 Mio. m³

PSW Wehr(980 MW)
Stauinhalt: 4,4 Mio. m³

PSW Säckingen (370 MW)
Stauinhalt: 2,2 Mio. m³

PSW Grimsel II (311 MW)
Stauinhalt: ... Mio. m³

PSW Hohenwarte II (320 MW
Stauinhalt: 3,3 Mio. m³

PSW Markersbach (1.050 MW)
Stauinhalt: 6,5 Mio. m³

PSW Goldisthal (1.060 MW)
Stauinhalt: 12,0 Mio. m³

PSW Kops II (450 MW)
Stauinhalt: 43 Mio. m³

BDEW Bundesverband der
Energie- und Wasserwirtschaft e.V.

Mathias Timm

Seite 1

b)

PSW-Projekte in Mitteleuropa

bdew
Energie. Wasser. Leben.

● Neubau
● Erweiterung

PSW Kühtai II
230 MW
Inbetriebnahme: 2016

PSW Heimbach
Neubau 400 bis 600 MW
Inbetriebnahme: 2019

PSW (SW Trier)
Neubau 300 MW
Inbetriebnahme: 2018

PSW Vianden
Erweiterung um 200 MW
Inbetriebnahme: 2013

PSW Forbach
Ausbau auf 270 MW
Inbetriebnahme: 2019

PSW Atdorf
ca. 1.400 MW
Inbetriebnahme: 2019

PSW Linthal
ca. 1.000 MW
Inbetriebnahme: 2015

PSW Nant de Drance
ca. 900 MW
Inbetriebnahme: 2016

PSW Puschlav
ca. 1.000 MW
Inbetriebnahme: 2018

PSW Waldeck II
Erweiterung auf 780 MW
Inbetriebnahme: 2016

PSW Schmalwassertalsperre
400 MW
Inbetriebnahme: ?

PSW Jochenstein-Riedl
300 MW
Inbetriebnahme: ca. 2018

PSW Feldsee
zusätzliche 140 MW
Inbetriebnahme: 2011

PSW Reißeck II
ca. 430 MW
Inbetriebnahme: 2014

PSW Limberg II / III
jeweils ca. 480 MW
Inbetriebnahmen: 2011 / 2016

PSW Gepatsch
ca. 390 MW

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Seite 2

Figure 12. (a) Pumped-storage power plants in Germany and neighboring states as well as (b) planned projects [32]; © BDEW; Stauinhalt: Water capacity; Inbetriebnahme: Beginning of operation.

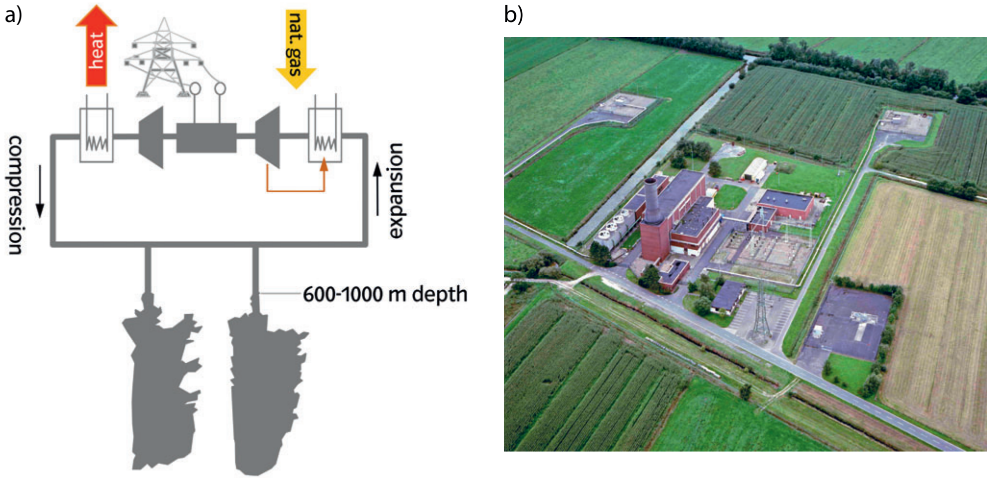


Figure 13. (a) Operating principle of a diabatic compressed-air reservoir and (b) view of the storage in Huntorf [34]; © Uniper SE.

321 MW [28] and a storage capacity of 2 h of full load at an electrical efficiency of 42 %. The McIntosh power plant in Alabama, USA, has been in operation since 1991 with an output of 110 MW and a storage capacity of 2860 MWh [29], equaling approximately 26 h of full load. The McIntosh power plant has a recuperator, which recovers the heat of the combustion offgas for preheating, thereby increasing the electrical efficiency of the plant to around 54 %. In contrast, adiabatic compressed-air energy-storage plants use a combination of a compressed-air reservoir and thermal storage (see Sect. 4.4) to store the heat of compression and make it available for decompression. Thereby, no external heat supply is needed. Adiabatic compressed-air energy storage plants are currently not applied on an industrial scale. However, they are being extensively studied in the ADELE and ADELA-ING projects (Fig. 14). The basis of these projects is a plant with an output of 90 MW and a capacity of 360 MWh aiming at an electrical efficiency of around 70 % [30].

The projects were able to demonstrate scientific and technological feasibility. Due to the current conditions of the electricity market, especially low spreads and low electricity prices, however, the cost effectiveness could not be demonstrated [33]. Large-scale implementation has been suspended until further notice.

4.1.3 Flywheels

In the case of flywheel storage, electrical energy is used to accelerate a flywheel. Conversely, it is discharged by deceleration of the flywheel. Flywheel energy storage is used locally and is characterized by high full-load cycle numbers and high efficiency. Flywheels exhibit high output power but only low capacity. The gyrating masses of conventional power plants can act as flywheels and thus represent a (small) independent storage capacity in the power grid (Fig. 15).

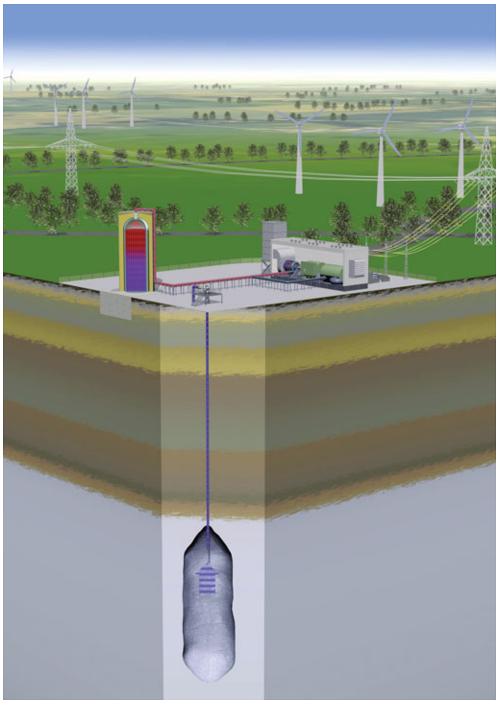


Figure 14. Operating principle of the adiabatic compressed-air accumulator Adele; © DLR [35].

4.1.4 Air Liquefaction as Mechanical Storage

While in the case of a compressed-air reservoir, cooling of the air during expansion in the turbine is a problem, this effect is exploited in the case of air liquefaction. The storage principle is based on the difference in volume between liquid and gaseous air. The production of 1 t of liquid air requires 439 kWh of energy, which can be reduced to 210–230 kWh by recycling cold released at the power recovery phase during the evapora-

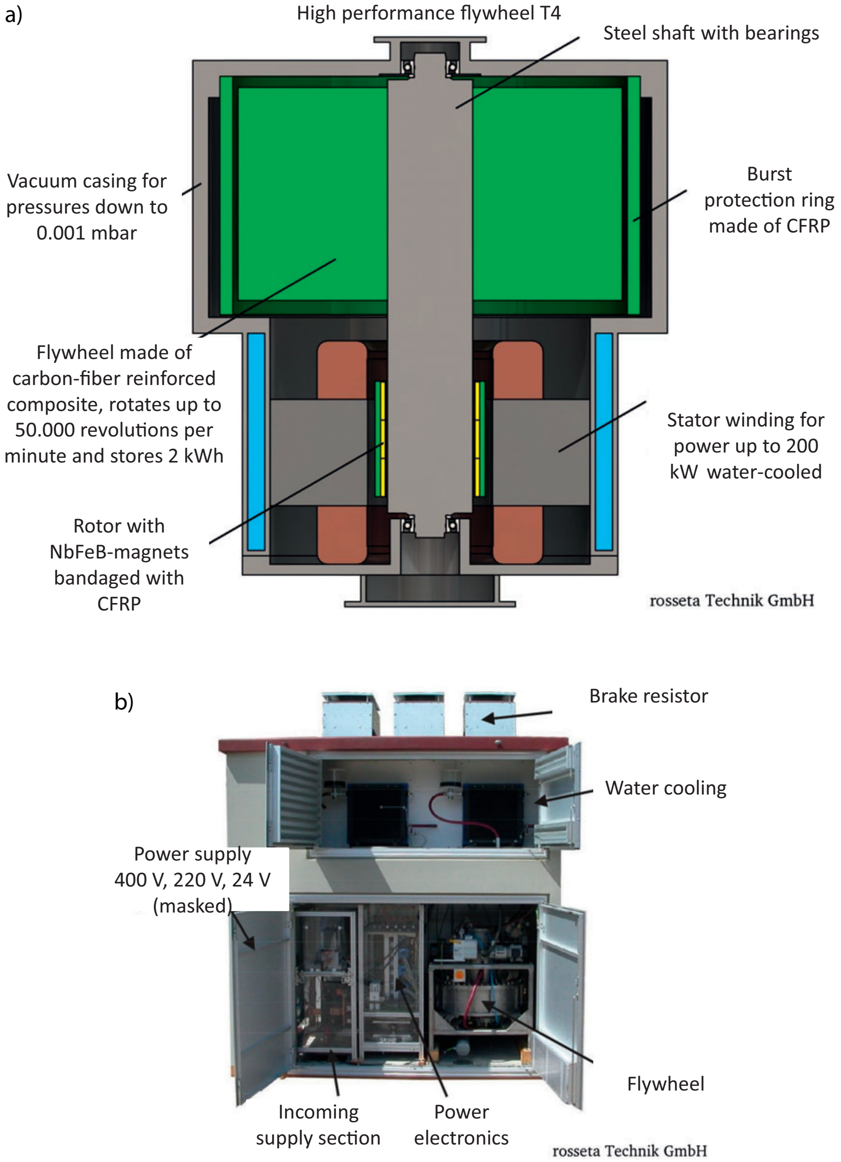


Figure 15. (a) Cross-section through a flywheel accumulator and (b) example of its technical implementation; © rosetta GmbH [37].

tion of liquid air. If oxygen and nitrogen are separated, 549 kWh are required to produce of 1 t of liquid nitrogen [36], which again can be reduced by recycling cold released during discharge.

By utilizing low-temperature heat and a turbine, the expansion of liquid air can achieve a heat-to-electricity efficiency of 50–60 %. For grid-scale systems a heat to power efficiency of around 75 % is expected. The high efficiency is made possible by the low temperature of liquid air. To achieve a high power output, either an external source of heat is required or heat produced at the compression stages of the air liquefaction process can be harvested and stored in thermal storage tanks for later use, enhancing the power output (Fig. 16). A pilot plant with an output of 350 kW has been successfully tested in Slough, UK [36], but has now relocated to the University of Birmingham. Highview and project partners, Viridor, were awarded funding from the UK government to build a 5 MW LAES technology demonstration plant. The plant is currently undergoing commissioning.

The pilot plant has successfully proven the concept of LAES technology and has already provided some services to the grid. The new 5 MW demonstration plant is expected to prove the technology at grid-scale. In principle, both nitrogen and air are feasible energy vectors. Since nitrogen storage would require an additional air separation unit, storage of liquid air has a relative economic advantage.

Due to the high energy demand, air-separation units are also suitable for storing energy in chemical processes (see Sect. 4.5).

4.1.5 Advantages of Mechanical Storage Systems

Mechanical storage systems have a number of advantages. They can be designed to cover a wide range of power input/output and storage capacity. The technologies are very robust and highly stable. Especially for the power grid they provide relatively inexpensive positive and negative balancing power and allow a restart of the collapsed power grid (black-start capability).

4.1.6 Disadvantages of Mechanical Storage Systems

Mechanical storage systems have a relatively low energy density. Therefore, they are almost exclusively designed and operated as large stationary installations (with the exception of flywheels).

4.2 Technologies for the Storage of Energy in the Form of Chemical Energy

For storing large quantities of power over extended periods of weeks to months, conversion to chemical energy storage is appropriate, mainly for reasons of convenience. The exploitation of the energy of chemical bonds enables high energy densities to be maintained, together with the possibility for storage in geological formations, which has advantages over other storage technologies in terms of space and cost. While various conversion chains are conceivable, the current debate focuses on hydrogen and its resulting conversion chains. The central underlying technology is water electrolysis, which employs electricity to split water into hydrogen and oxygen.

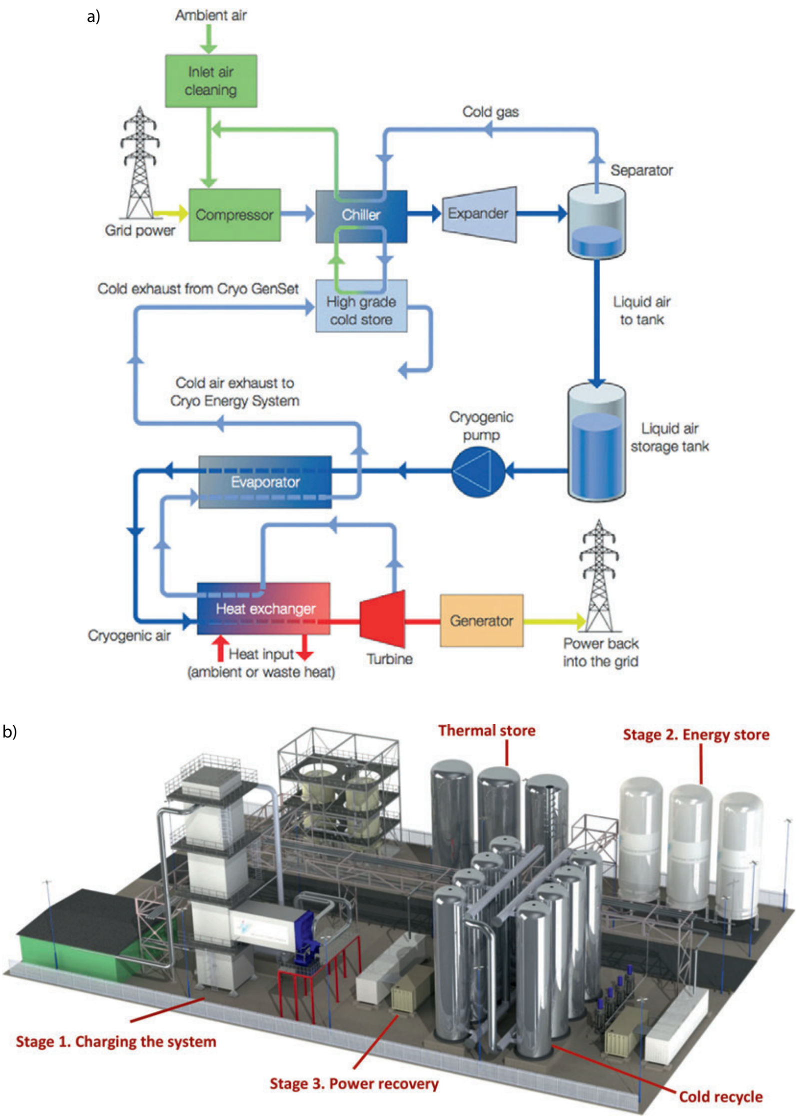


Figure 16. (a) Schematic representation of the use of air liquefaction as electricity storage [38] and (b) plant design [39]; © Highview Power Storage.

4.2.1 Production of Hydrogen from Renewable Energy in Electrolytic Processes

For the production of hydrogen from water and electricity various electrochemical processes are possible. All are based on the splitting of water into its hydrogen and oxygen constituents by applying an electrical voltage. Thus, this is technically comparable to a fuel-cell system operating in reverse direction to the current flow. The electrolytic processes considered here are alkaline, proton-exchange membrane (PEM), and high-temperature electrolysis. The costs of hydrogen produced in this manner are dependent on the investment costs of the electrolyzer, the scenario under consideration, the resulting full-load hours per year, and the operating costs, especially the costs of procuring the required electricity.

Alkaline Electrolysis

Alkaline electrolysis is already used for the production of hydrogen on an industrial scale. Production rates can reach up to 740 m^3h^{-1} per stack and up to 30 000 m^3h^{-1} for total plants [15]. In industrial settings, 20–40 % KOH solution is used at an operating temperature of 70–90 °C to reduce the overpotential [40]. The anode and cathode areas are separated by a diaphragm, allowing the KOH solution to transport the OH^- ions. At the cathode, water is cleaved into H_2 and OH^-, and the latter is converted to O_2 and H_2O at the anode. Catalysts are usually composed of nickel, cobalt or iron. The current densities present under operating conditions are generally between 0.2 and 0.4 A cm^{-2} [40].

Anode:	$2\,OH^- \rightarrow 0.5\,O_2 + H_2O + 2\,e^-$
Cathode:	$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^-$
Overall reaction:	$H_2O \rightarrow H_2 + 0.5\,O_2$

This process is used in the chemical industry when particularly pure hydrogen is required for further synthesis in quantities for which the steam reforming of natural gas is not yet economical. The most efficient alkaline electrolysis systems require about 4.3 kWh of electricity to produce 1 m^3 of H_2 [15]. This corresponds to an efficiency of 80 % based on the higher heating value or 70 % based on the lower heating value of the hydrogen produced. The remaining electrical energy is required to compensate for the overpotential or is consumed by ohmic losses and therefore is lost as heat. The currently operating plants are designed to run at an optimum constant operating point. Essentially, the technology allows the use of plants to compensate for short-term power fluctuations, but the minimum partial load is limited to about 20–40 % of the nominal load [41]. At low partial load, the hydrogen diffusing through the diaphragm results in potentially unsafe contamination of the oxygen. While many systems produce hydrogen at atmospheric pressure, the technology can also be used to obtain hydrogen at elevated pressure (up to 30 bar). Already today, electrolyzers with lifetimes of up to 90 000 h (> 10 a) are in use [42].

Research priorities in the field of alkaline electrolysis lie especially in the area of increasing power density with catalysts that operate with lower overpotentials and membrane materials with reduced resistance. The aim is to reduce investment costs from the current installed capacity of approximately 1000 € kW^{-1} to 500 € kW^{-1} by increasing the power density and reducing the material costs [40, 41]. Furthermore, by using new diaphragms with lower H_2 diffusivity, a minimum partial-load capability of <10 % should be achievable [41] (Fig. 17).

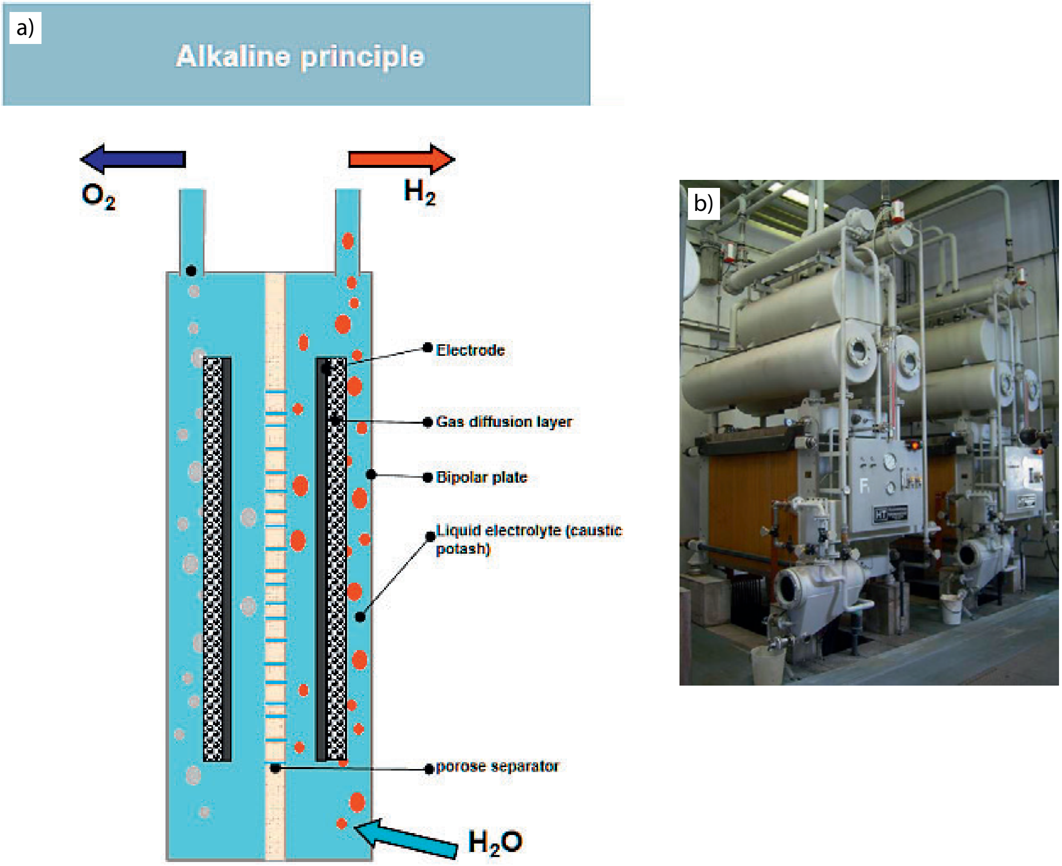


Figure 17. (a) Operation principle [43], © SIEMENS, and (b) technical implementation of alkaline water electrolysis [44], © HT Hydrotechnik.

PEM Electrolysis

Having only undergone about 20 years of development, PEM electrolysis (Fig. 18) is a relatively young technology based on the use of a proton-conducting polymer membrane (proton-exchange membrane, PEM). Thus, pure water can be used and the periphery can be reduced in comparison to alkaline electrolysis since processing of the base is eliminated. Water splitting occurs on the anode side of the PEM.

Anode: $H_2O \rightarrow 2\ H^+ + 0.5\ O_2 + 2\ e^-$

Cathode: $2\ H^+ + 2\ e^- \rightarrow H_2$

Overall reaction: $H_2O \rightarrow H_2 + 0.5\ O_2$

As catalysts, expensive precious metals such as platinum and iridium are currently used. The efficiencies achieved are in the same order of magnitude as for alkaline electrolysis, although much higher current densities of 0.6–2.0 A cm^{-2} are reached, which enables a more compact design [40].

With regards to linkage with volatile renewable energy, the PEM electrolyzer is characterized by excellent dynamic response and a minimum partial load of < 5 %. In addition, the PEM electrolyzer allows overload operation of up to 300 %. Although this causes a reduction in efficiency due to increased ohmic losses, the capacity to be installed is significantly reduced in the case of buffering volatile power generation, since extreme power peaks are limited to only a small number of hours per year. Furthermore, PEM electrolysis can be designed for pressure ranges of up to 100 bar. Currently, demonstration plants of up to 50 m^3h^{-1} are being operated to gather operational experience. The objective of facilities in the megawatt power range from 2015 onwards was reached with the construction of the Energiepark Mainz, which contains 3 electrolyzers with a peak power of 2 MW, opening up production ranges of > 200 m^3h^{-1}.

Research in the field of PEM electrolysis is especially focused on cost reduction. To this end, several lines of research address a reduction of the catalyst load or the use of alternative catalysts. In addition, the cost of flow fields and separators account for up to 50 % of the stack costs and provide another lever for cost reduction [42]. The investment costs today (>2000 € kW^{-1} installed capacity) should be reduced to less than 600 € kW^{-1} installed capacity [40, 42]. Further research will address the long-term stability and the scale-up of stacks as well as the periphery in the megawatt range.

High-Temperature Electrolysis

High-temperature electrolysis (solid-oxide electrolysis cell, SOEC) has so far only been used on a laboratory scale for research purposes and is not used industrially. Analogous to

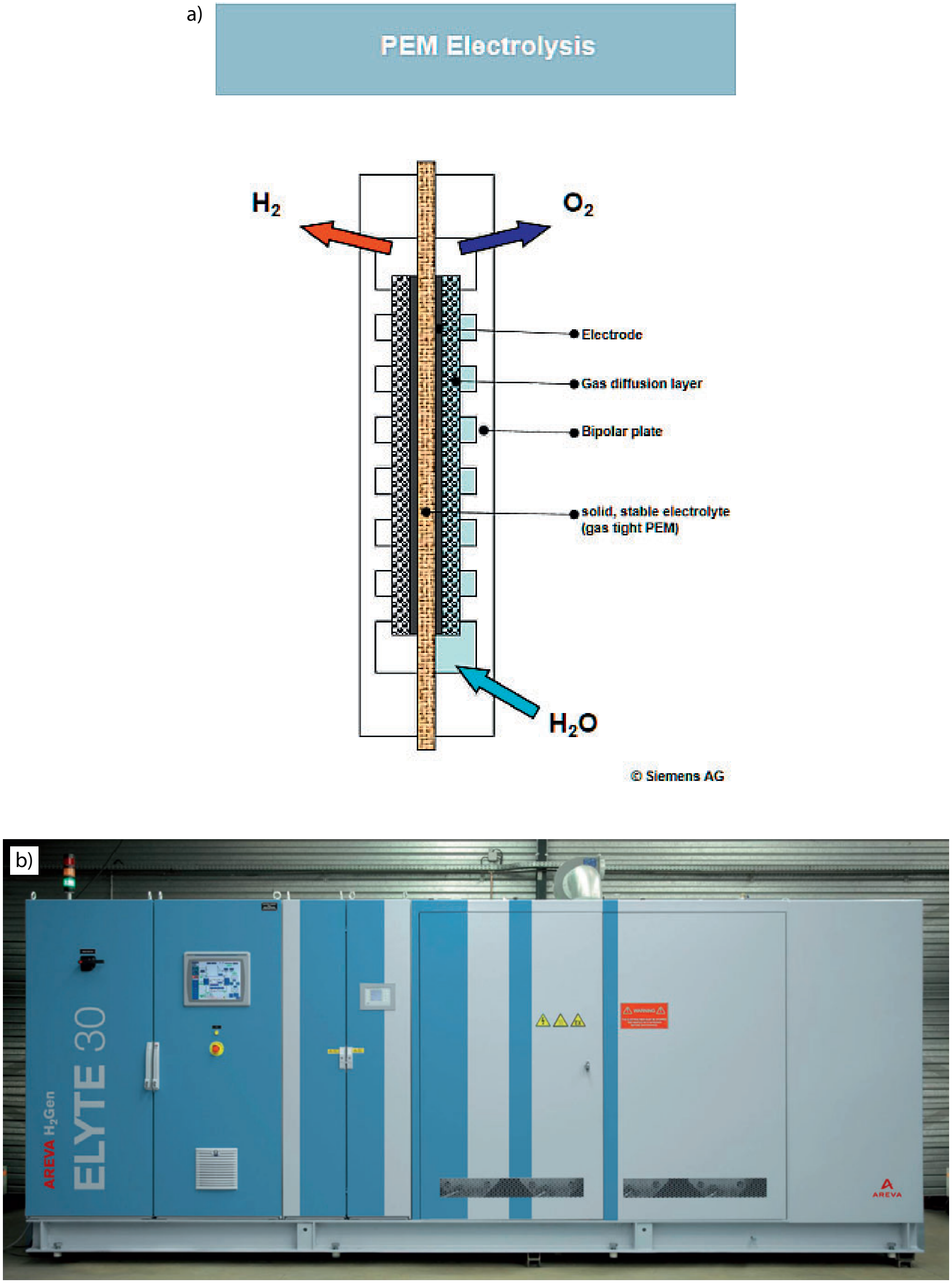


Figure 18. (a) Operating principle of PEM electrolysis [43], © SIEMENS, and (b) example of its technical implementation [45], © AREVA H2Gen GmbH.

the solid-oxide fuel cell (SOFC) it is based on an oxygen-ion-conductive ceramic. In contrast to the low-temperature electrolysis processes described above, an SOEC is operated at temperatures between 700 and 1000 °C [40]. The advantage here is that the standard free enthalpy ΔG of the reaction decreases with increasing temperature (Fig. 19 a). Thus, at higher temperatures, the power requirements decrease, but at the same time part of the reaction enthalpy ΔH must be provided by heat sources. Hence, it is possible that at certain operating temperatures only about 2.6 kWh of electricity is required for the production of 1 m^3 of H_2 [42].

Anode:	$O^{2-} \rightarrow 0.5\ O_2 + 2\ e^-$
Cathode:	$H_2O + 2\ e^- \rightarrow H_2 + O^{2-}$
Overall reaction:	$H_2O \rightarrow H_2 + 0.5\ O_2$

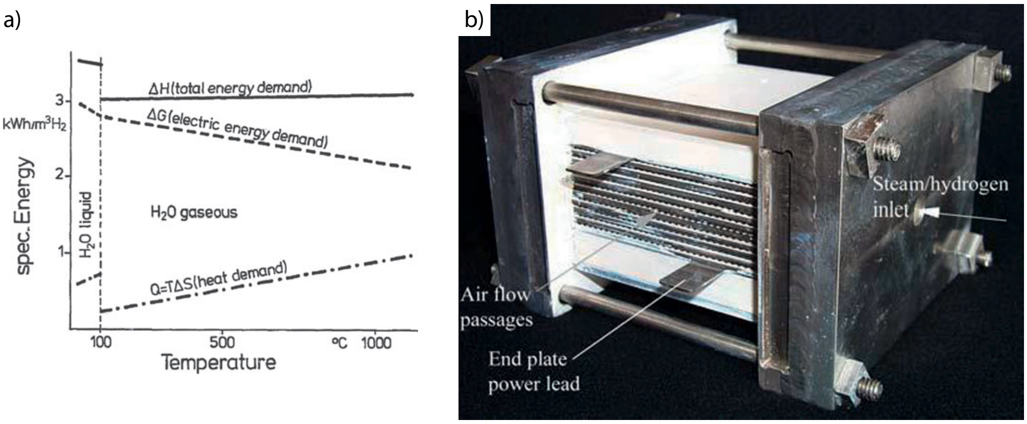


Figure 19. (a) Progression of thermodynamic functions for the electrolysis of water as a function of temperature according to Erdle et al. [47] and (b) example of a HT-electrolysis stack [48]; © DoE.

In November 2014, a power-to-liquid plant was opened in Dresden by the company Sunfire, combining high-temperature electrolysis with a downstream Fischer-Tropsch (FT) process for the production of synthetic fuels [46].

Operation of Electrolyzers

The operating mode of an electrolyzer defines the contribution it can make to balancing energy. The normal operating mode of an electrolyzer is aimed at maximum production of hydrogen at constant power supply. Such an operating mode only allows a positive contribution to balancing energy by throttling the system, resulting in lower hydrogen production rates. Electrolysis could also be used to take up surpluses, thereby providing retrievable balancing power for the electricity grid. If the system is operated between full load and standby, it can, through regulation of the operation, provide both positive and negative balancing power for the electricity grid with corresponding fluctuations in hydrogen production. Modern electrolytic methods, to which both alkaline and PEM electrolysis belong, are sufficiently flexible and resilient to compensate for relatively rapid fluctuations in available power, e.g., due to changes of windpower available.

It should be kept in mind, however, that the efficiency of the system very much depends on the number of operating hours and the amount of hydrogen generated. The systems currently in operation are designed for maximum hydrogen production and not for grid-friendly operation. The hydrogen currently produced is not used as an energy carrier, but as a chemical in the chemical industry's supply chain. Electrolyzers are operated according to order books and not according to balancing-power demand.

4.2.2 Thermal Processes for Hydrogen Production

Thermal Water Splitting

An alternative to electrolysis is based on the fact that at very high temperatures water is dissociated into its components, hydrogen and oxygen. In the past, extensive research activities have been performed to this end, especially the "Adam and Eve" project, the objective of which was the use of high-temperature heat from nuclear power plants of the fourth generation for water splitting. The fundamental problem of a reliable separation of the hydrogen/oxygen mixture could not be conclusively resolved in a technically satisfactory way. The temperatures necessary for the thermal splitting of water can also be generated by concentrated solar radiation (concentrated solar power, CSP).

Thermochemical Cycle Processes for Water Splitting

The direct thermal splitting of water or CO_2 requires temperatures above 2000 °C [49], with accordingly high performance specifications for all materials used. The temperature can be significantly reduced through the use of thermochemical cycle processes. For this purpose, a redox pair is used as catalyst. This is illustrated below in a two-step process for water splitting with a metal oxide pair:

1. Water splitting: $MO_x + H_2O \rightleftharpoons MO_y + H_2 (x < y)$

2. Regeneration: $MO_y + \text{heat} \rightleftharpoons MO_x + 1/2\ O_2 (x < y)$

Overall reaction: $H_2O + \text{heat} \rightarrow H_2 + 1/2\ O_2$

In this cycle, oxygen and hydrogen production can be separated spatially. In the cold part of the process ($T \approx$ 800–900 °C), hydrogen is formed while in the hot part ($T \approx$ 1200 °C), oxygen is removed from the oxide. A variety of material combinations can be used, e.g., Fe_3O_4/FeO, TiO_2/TiO_x, Mn_3O_4/MnO, CeO_2/Ce_2O_3, Co_3O_4/CoO, Nb_2O_5/NbO_2, In_2O_3/In, WO_3/W, and CdO/Cd [50]. For use as a solid, the melting point of the Fe_3O_4/FeO system must be increased to above the reduction temperature (reaction 2 in the above cycle) by partial substitution of iron in the metal lattice by other metals. Then ferritic materials with spinel structure, such as $ZnFe_2O_4$, $NiZnFe_2O_4$, $MnFe_2O_4$, and $CoFe_2O_4$, can be used in in the form of supported nanoparticles [51].

In addition to the cyclic processes based on metal oxides, other redox couples can also be used. For example, the sulfur/iodine cycle [50], also used for the production of hydrogen, only requires an upper temperature of approximately T = 850 °C:

1. Hydrolysis of SO_2: $I_2(l,g) + SO_2(g) + 2\,H_2O(g) \rightleftharpoons 2\,HI(g) + H_2SO_4(l) + \text{heat}$ $(T = 120\,°C)$
2. Oxygen production: $H_2SO_4(g) + \text{heat} \rightleftharpoons SO_2(g) + H_2O(g) + 0{,}5\,O_2(g)$ $(T = 800 - 1000\,°C)$
3. Hydrogen production: $2\,HI(g) + \text{heat} \rightleftharpoons I_2(g) + H_2(g)(T = 450\,°C)$

Overall reaction: $H_2O + \text{heat} \rightarrow H_2 + 1/2\,O_2$

Besides the purely thermal cycle processes, energy can also enter the reaction in a different way. An example is the hybrid sulfur cycle [44], which requires electrical energy in addition to thermal energy:

1. Hydrogen production: $SO_2(aq) + 2\,H_2O(l) + \text{electricity} \rightleftharpoons H_2SO_4(aq) + H_2(g)$ $(T = 80 - 120\,°C)$
2. Oxygen production: $H_2SO_4(g) + \text{heat} \rightleftharpoons SO_2(g) + H_2O(g) + 0{,}5O_2(g)$ $(T = 850\,°C)$

Overall reaction: $H_2O + \text{electricity} + \text{heat} \rightarrow H_2 + 1/2\,O_2$

In addition to hydrogen production, other reactions may also be represented as thermal cycles. Thus, the splitting of carbon dioxide into carbon monoxide and oxygen can be carried out in a similar manner to the splitting of water:

CO_2 decomposition: $MO_x + CO_2 \rightleftharpoons MO_y + CO(x < y)$

Regeneration: $MO_y + \text{heat} \rightleftharpoons MO_x + 1/2\,O_2(x < y)$

Overall reaction: $CO_2 + \text{heat} \rightarrow CO + 1/2\,O_2$

The combination of cyclic processes for water and carbon dioxide splitting allows the thermochemical preparation of synthesis gas based on carbon dioxide, water, and heat.

Moreover, the production of other substances is a current research topic. Thus, the production of ammonia via a thermal cycle with chromium compounds is discussed, whereby hydrogen or carbon monoxide could be used as a reducing agent [52]:

1. Nitride formation: $2\,Cr(s) + 0{,}5\,N_2(g) \rightleftharpoons Cr_2N(s)$ $(T \approx 1000\,°C)$
2. Corrosion: $Cr_2N(s) + 3\,H_2O(g) \rightleftharpoons Cr_2O_3(s) + NH_3(g) + 3/2\,H_2(g)$ $(T \approx 1000\,°C)$
3. Reduction: $2\,Cr_2O_3(s) + 3\,H_2(g) \rightleftharpoons 2\,Cr\,(s) + 3\,H_2O(g)$ $(T \approx 1200 - 1600\,°C)$

Overall reaction: $1/2\,N_2 + 3/2\,H_2 \rightarrow NH_3$

In particular, the hydrolysis reaction of Cr_2N (reaction 2 in the above scheme) does not perform satisfactorily. Whether the process will achieve a technical relevance is therefore currently not foreseeable.

The thermal cycle processes can be performed with any adequate heat source. A major focus of current research and development activities lies in the use of concentrated solar radiation [51] as a heat source. Since direct sunlight, if possible without interruption, must be available, this method is currently inferior to electrolysis using electricity from photovoltaics and wind turbines due to the typical weather conditions in Germany. However, this does not necessarily hold for sunny locations in North Africa, the Middle East, and parts of southern Europe.

4.2.3 Hydrogen Production by the Kværner Process

In 1990, Kværner presented the carbon black and hydrogen process, in which plasma pyrolysis converts hydrocarbons (from light gases to heavy oil residues) to hydrogen and carbon black without residue. In 1992, a pilot plant was put into operation to test the method on an economically significant scale [53], and in 1999, the first commercial plant was started. Here, hydrogen is the coproduct to carbon black. Accordingly, the economic valuation of the plant is oriented towards the carbon black market, mainly for the plastics sector and metallurgy. Formally, the reaction of the Kværner process runs according to the following equation:

$$C_xH_y + \text{plasma} \rightarrow x\text{C (carbon black)} + y/2\,H_2$$

In addition, steam is produced for heat dissipation.

4.2.4 Methane Pyrolysis

The decomposition of methane is an emerging route towards the production of hydrogen with a low carbon footprint. Methane or other lower hydrocarbons are decomposed in a high temperature pyrolysis process generating hydrogen and solid carbon [54]. It can be summarized as:

$$CH_4 \rightarrow 2H_2 + C, \quad \Delta H_R^0 = 37.4\text{kJ mol}^{-1}H_2$$

Different technical approaches are followed and R&D and pre-commercial projects, e.g., thermal decomposition by a consortium of BASF, Linde and ThyssenKrupp [55] as well as plasma pyrolysis by the US-based company Monolith [56] are ongoing. Other approaches include thermocatalytic decomposition [57] or liquid metal processes [58].

4.2.5 Options for Conversion of Hydrogen to other Energy Forms

Instead of using hydrogen directly as fuel, it is also possible to convert it to other forms of energy and thus, e.g., to use existing infrastructures. Thus, by reaction with (possibly biogenic) CO_2, the hydrogen can be converted to methane, methanol, higher fuels, or chemicals. In the economic evaluation of different process chains, it should be kept in mind that a substantial part of the costs of the entire system are due to the electrolyzer. Different investment costs for additional process steps (e.g., methanation, methanol synthesis, Fischer-Tropsch process) are therefore comparatively less significant than if world-scale facilities for such processes were implemented based on natural gas.

Conversion of Hydrogen to Methane and Use in the Energy System

Through methanation hydrogen and CO_2 can be converted to methane [59]. If the methane is produced predominantly (>80 %) by using electricity generated from renewable resources and renewable CO/CO_2, then in accordance with the Energy Act §3 No. 10c with respect to feed priorities, it is considered equivalent to biogas [60].

The conversion of hydrogen with CO_2 to methane is formally described by the following catalyzed reaction:

$$4\ H_2 + CO_2 \rightleftharpoons CH_4 + 2\ H_2O, \quad \Delta H_R^0 = -165\ \text{kJ mol}^{-1}$$
$$(T = 300\ ^\circ\text{C}, P = 30\ \text{bar})$$

Conversion to methane makes it possible to use the existing gas grid and the associated underground storage, albeit with the disadvantage of an additional process step and the corresponding conversion losses. If an additional adjustment in heating value is desired, a side stream can be converted to higher hydrocarbons by a Fischer-Tropsch process. As an ideal replacement for natural gas, applications are reconversion via a power plant, use as a fuel to generate heat, possibly feeding into district heating and steam systems, and use as a fuel for gas-powered vehicles as well as chemical feedstock.

Methanation via syngas from fossil feedstocks has been technically implemented several times already. An overview of the detailed technical requirements and options was created as part of a DVGW (German Association for Gas and Water) project [61]. The use of CO_2 from biogas with or without prior removal of the biomethane is possible, but also defines the dimensions of the system, whereby different process concepts are conceivable.

Conversion of Hydrogen to Methanol and Use in the Energy System

Hydrogen can react with CO_2 to form methanol in a catalytic reaction:

$$3\ H_2 + CO_2 \rightarrow CH_3OH + H_2O,$$
$$\Delta_R H_0 = -131.2\ \text{kJ mol}^{-1}, \Delta_R H_U = -87.3\ \text{kJ mol}^{-1}$$

This process is well known and is used worldwide in mega scale industrial plants, i.e., plants with $1 \times 10^6\ \text{t a}^{-1}$ production volume. To use this reaction for the exploitation of surplus electricity from renewable energy, in the foreseeable future, significantly smaller plants with production volumes up to $20\,000\ \text{t a}^{-1}$, with reduced economic efficiency, are needed.

The reasons for this are the expected relatively small amounts of actually existing inexpensive surplus power as well as its local (off-shore wind farms) and temporal distribution (load peaks). The latter requires temporal buffering of the intermediate product hydrogen in larger storage units in order to allow continuous operation of the downstream methanol plant.

Liquid methanol can easily be transported by road, rail, and pipeline and can therefore also transport renewable energy over long distances.

The renewably generated green methanol could be applied in the following areas of the energy sector:

- Direct use as fuel additive: Methanol can be safely added to gasoline fuels and standard-compliant volume fractions reach up to 3 %. Modern internal combustion engines tolerate up to 10 % methanol. Compared to gasoline, the specific energy density of methanol is only half as high. This drawback can, however, be offset by the much better efficiency, resulting from the possibility of considerably higher compression, which leads to significantly higher engine performance.
- Use in gas turbines (reconversion): The efficiency of a gas turbine operated with methanol is 9 % higher [62] compared to methane.

In addition, its use as a base chemical in processes of the chemical industry is possible.

Conversion of Hydrogen to Hydrocarbons and Use in the Energy System

Liquid hydrocarbons are expected to remain in demand in the future for the propulsion of aircraft and vehicles owing to their high energy densities and the existing infrastructure. Nonfossil liquid hydrocarbon fuels can be produced by reaction of H_2 with an appropriate carbon source. As carbon source CO_2 as well as various types of biomass within the framework of biorefineries can be considered. The quality of the products from catalytic synthesis (e.g., Fischer-Tropsch process) allows the replacement and unlimited addition to today's petroleum fuels.

The reaction of hydrogen with CO_2 to form liquid hydrocarbons comprises two heterogeneously catalyzed partial steps according to the following formal reactions:

$$\text{CO}_2\ \text{conversion:} \quad nH_2 + nCO_2 \rightleftharpoons nCO + nH_2O \tag{1}$$

$$\text{Fischer-Tropsch:} \quad (2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \tag{2}$$

$$\text{Overall reaction:} \quad (3n+1)H_2 + nCO_2 \rightarrow C_nH_{2n+2} + 2nH_2O \tag{3}$$

Target products corresponding to modern liquid fuels:

n = 10 – 14: kerosene for gas turbines

n = 5 – 20: fuels for piston engines

Alternative or complementary routes for the integration of hydrogen into the production of liquid hydrocarbons include hydrogenation of vegetable oils or novel algae oils that do not compete with food or feed and admixture to low-hydrogen synthesis gases from the gasification of lignocellulosic biomass according to Eq. (2).

The production of liquid hydrocarbons from fossil fuels (natural gas, coal) by the Fischer-Tropsch process is currently performed in large plants. The worldwide largest one is the PEARL GtL plant operated by Shell and located in Qatar.

Processing wellhead gas from the world's largest single nonassociated gas field, the PEARL GtL plant produces up to 140 000 barrels of oil per day [63]. Many years of experience are available for transfer to the nonfossil carbon sources discussed here. The properties of the produced hydrocarbons can be adjusted with respect to low-emission combustion in technical combustion systems (engines, gas turbines). In the case of vegetable oil as raw material, hydrogenation to high-quality kerosene or diesel fuel takes place in large plants with fossil-based hydrogen. The associated CO_2 emissions can be avoided by using electrolytic hydrogen from renewable electricity.

Comparison of the Process Chains via Methane and via Methanol

Currently, a 4000 t a^{-1} methanol plant is operated in Iceland and a 2000 t a^{-1} pilot plant for methane in Germany.

Iceland

In 2012, the power-to-liquid process chain from renewable energies to methanol was demonstrated in the George Olah Renewable Methanol Plant in Iceland, which has many special features due to its young geologic history. The \$ 8 million plant based on the emissions-to-liquid (ETL) process [64] is designed for the production of 5 million L a^{-1} (about 4000 t a^{-1}), which is equivalent to a CO_2 turnover of 5400 t a^{-1}. The pilot plant serves as a basis for expanding the investment concept to 50 million L a^{-1} (ca. 40 000 t a^{-1}). The plant operates completely with renewable energy. The CO_2 is recovered from a geothermal stream. The consumption of electric energy for water electrolysis, covered by geothermal energy, corresponds to a constant power of 5 MW. The methanol is mixed with gasoline and can cover up to 2.5 % of Iceland's gasoline demand.

Germany

The complete process chain of renewable energy to methane was first demonstrated by Audi as part of the e-gas project. The plant in Werlte uses wind turbines with a maximum output of 6 MW to dynamically operate water electrolysis. In a methanation reactor, the resulting hydrogen and separated CO_2 from a neighboring biogas plant are converted to methane, which can be fed directly into the natural gas grid. The resulting heat from the methanation is used to supply the attached biogas plant with process heat. The plant is designed for production of 1000 t a^{-1} methane, which stoichiometrically converts 2800 t of CO_2 [65, 66]. The gas is substituting fuel withdrawn by natural gas-powered vehicles.

The plant in Werlte operates under highly fluctuating conditions and benefits from the well-developed natural gas infrastructure. The use of wind power for mobility in the form of natural gas vehicles appears only on the balance sheet becauses the given natural gas vehicles are supplied through the general natural gas grid. An overview of the current power-to-gas projects in Germany, with and without methanation, has been compiled as a map [67].

Figs. 20 and 21 exemplarily describe an efficiency assessment of the process chains with a subsequent reconversion of methane and methanol in a modern cogeneration plant. The efficiencies used herein are estimates and do not claim to replace a detailed individual analysis.

Methanation is an exothermic process and thus is associated with waste heat. The maximum efficiency (LHV) is 83 %. Since methanation is carried out at 230–780 °C, depending on the process [61], the waste heat accumulates at a temperature level which makes it suitable for use in other processes. The most obvious one is the coupling of the methanation with the treatment of CO_2, e.g., from biogas, in adsorption processes. In this case, the waste heat from methanation is sufficient to perform the energy-intensive step of desorption of CO_2. In the overall energy balance of the power-to-gas concept, this does not result

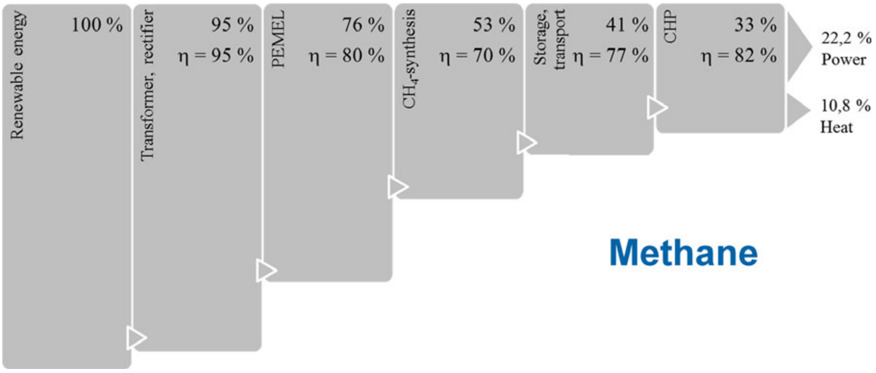


Figure 20. Efficiency chain for the conversion of renewable electricity to methane and its use. The losses in storage and transport are mainly due to the compression and recompression of the gas [62].

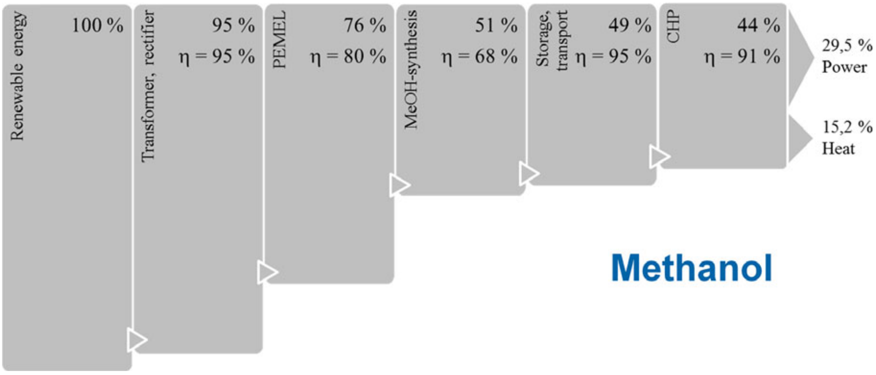


Figure 21. Efficiency chain for the conversion of electricity from renewable sources to methanol and its use [62].

in further reduction of efficiency, considering the availability of CO_2.

CO_2 Sources

Further conversion of electrolytically generated hydrogen to methane, methanol, or Fischer-Tropsch fuels requires a CO_2 source for which the supply of CO_2 is matched to the expected production of hydrogen. Tab. 6 compares different CO_2 sources and conversion technologies.

Conversion of Hydrogen to Ammonia

Ammonia plays a special role in the discussion. Technically, its use as an energy source is possible and was successfully demonstrated in pilot projects. Ammonia has similar properties like propane and can be used as chemical energy storage. A new concept efficiently combines ammonia production for electricity storage, coupled to an SOEC fuel cell to deliver electricity back to the grid [69]. This concept is a good example on how a combination of different transformation process steps delivers an effective energy storage functionality. Another project has emerged in the Netherlands [70] with the focus on storing ammonia produced with renewable energy and using it to power gas turbines when electricity is required. There is also work on thermochemical production of ammonia [71]. However, the main use of ammonia today lies in the production of fertilizers. The use of ammonia as an energy source would therefore link the fertilizer market and the global supply of food and feed even more strongly with the energy markets.

4.2.6 Storage and Transport of Energy Storage Materials

Storage and Transport of Hydrogen

The majority of currently produced hydrogen is so-called captive hydrogen, which is produced locally for further use on the same industrial site. As a result, only a small amount of hydrogen is transported. If large quantities of hydrogen are to be produced from surplus power, it is likely to happen at different locations, e.g., near large wind farms, in relatively small amounts with respect to industrial consumption. This raises the question how the hydrogen can be transported to a consumer. There is experience with hydrogen infrastructure to which one can resort. Larger plants were previously housed in chemical sites or refineries that had the necessary know-how in dealing with hydrogen to ensure safe handling. However, a long-range, decentralized hydrogen production has different requirements.

Hydrogen Storage in Cavern Storage Systems

Small quantities of hydrogen can be stored above ground in spherical storage tanks. For the storage of large amounts of hydrogen, caverns are used at pressures of 13.5 MPa. There is already long-standing, positive experience in the USA and UK [72]. For cavern storage suitable salt formations are found primarily in northern Germany. Potentially, there is a long-term competition for usage of subterranean formations for compressed-air and hydrogen storage, which could alternatively be used for petroleum or natural gas storage. Currently, the following hydrogen reservoirs are in use [73]:

- Teeside, UK, operator SABIC Petrochemicals, 3 × 70 000 m^3, 4.5 MPa (const.), 25 GWh, operational experience ca. 30 years (originally ICI);
- Clemens Dome, Lake Jackson, Texas, USA, operator Conoco Philips, 580 000 m^3, 7–13.5 MPa, 92 GWh, since 1986;
- Moss Bluff Salt Dome, Liberty County, Texas, USA, operator Praxair, 566 000 m^3, 7.6–13.4 MPa, 80 GWh, since 2007.

Transport of Hydrogen in Pipelines

In Germany, sufficient historical experience exists in the handling of hydrogen-rich gases in gas grids. For decades, Air Liquide has successfully operated an approximately 240 km-long pipeline network in the Rhine Ruhr area and a 200 km-long pipeline network for hydrogen in the Benelux countries (Fig. 22). Linde AG operates an approximately 100 km-long hydrogen pipeline network in central Germany (around the industrial site Leuna). In addition, chemical and refinery sites have local hydrogen networks and possess relevant experience. It can therefore be assumed that hydrogen can be safely handled and transported in appropriate pipeline grids.

Transport of Hydrogen by Road and Rail

Small quantities of hydrogen can be transported in tankers as pressurized gas or liquefied (at –253 °C). Even then, however, the volumetric energy density is significantly lower than that of other liquid fuels.

Future Transportation Options for Hydrogen

In addition to the transport and storage of hydrogen as a gas under pressure or in its liquid state, certain organic carrier

Table 6. CO_2 sources and stoichiometric volume flows of power-to-gas and power-to-liquid [68] as well as own calculations under standard conditions (298.15 K, 101 300 Pa). For comparison: An alkaline electrolysis stack has a volumetric flow rate of 740 m^3h^{-1} H_2.

		Methanation		Methanol production		Fischer-Tropsch fuels	
CO_2 source	CO_2 source flow [m^3h^{-1}]	H_2 flow [m^3h^{-1}]	CH_4 [m^3h^{-1}]	H_2 flow [m^3h^{-1}]	CH_3OH [$t\,h^{-1}$]	H_2 flow [m^3h^{-1}]	$-CH_2-$ [$t\,h^{-1}$]
Biogas plant	500	2000	500	1500	0.7	1500	0.3
Biomass gasification	2100 (+1400 CO)	8400 (+4200)	2100 (+1400)	6300 (+2800)	2.8 (+1,8)	6300 (+2800)	1.2 (+0,8)
Ammonia plant	30 000	120 000	30 000	90 000	39	90 000	17
Coal-fired power plant (500 MW, 930 g kWh^{-1})	240 000	960 000	240 000	720 000	314	720 000	137

Figure 22. Integrated pipeline network of Air Liquide in the Benelux countries. The red lines represent hydrogen pipelines [74]; © AirLiquide.

molecules can be used. The chemical basis for this is a combination of reversible hydrogenation and dehydrogenation reactions. The hydrogen reacts chemically with the carrier molecule and can then be transported in the form of a liquid. Hydrogen release, with regeneration of the carrier molecule, then takes place at the application site of the hydrogen. Currently, the most technologically mature method is the Chiyoda process [75], based on the reaction system toluene/methylcyclohexane, which has very low conversion losses, but is only suitable for large-scale application. Processes based on carbazole derivatives [76] or dibenzyltoluene [77] are also under consideration. The original works in the framework of a research project of the DoE [78] have again been taken up and further developed in Germany. In these systems, the local stationary or mobile application is the focus of the considerations. Regardless of the individual system, the focus lies on making hydrogen transportable in a liquid form, in order to use the existing unpressurized transport infrastructure with only minimal changes (tank trucks, ships). Similar to the transport of liquid hydrogen, liquid organic hydrogen carriers (LOHC) can also be used for the safe storage of hydrogen. In this case, the considerations are also aimed at mobile and local use of hydrogen in fuel cells to generate electricity or for combined heat and power generation in small cogeneration plants.

Natural gas Grid

In the past, hydrogen-containing gases, e.g., town gas, were used in parts of the gas grid. Currently, the introduction of hydrogen up to a limit of 5 vol % is allowed by the technical regulations [79]. The limits for hydrogen must be met not only for feed-in, but at any point in the grid. This requires a correspondingly sufficient volume flow of natural gas, not only at the feed point, but also at the following regions of the grid. At the end of 2013, the first direct injection of hydrogen into the gas distribution system took place [80]. There is already experience in industrial gas networks (chemicals, steel) with transport and storage of gases with high hydrogen contents. Regulations still limit the hydrogen content in compressed natural gas (CNG) for use in natural gas vehicles to 2 % [81, 82].

The suitability of the gas system and its peripherals for gas compositions with higher concentrations of hydrogen is currently the subject of lively discussion. The final report of DVWG on the hydrogen tolerance of the natural gas infrastructure [83] concludes that the infrastructure would in principle function with an increased limit of 10 % hydrogen content in the natural gas, with exceptions in the area of natural gas filling stations and some industrial applications. Gas turbines, porous reservoirs, completion equipment, completion equipment/above-ground plants, CNG1 tanks (vehicles), and large burners were identified as critical components of the infrastructure requiring adaptation.

Hydrogen has a lower calorific value and different combustion characteristics compared to natural gas. The compressors in the natural gas grid must be adapted to the new composition and provide a correspondingly higher compression performance to ensure the same (energy) transport capacity in the grid.

Natural gas is stored in cavern and pore storage facilities. Hydrogen storage in caverns does not have additional requirements. Pore storage, however, has a high ratio of surface area to volume. This is a good basis for microbiological processes that can utilize the stored hydrogen. This can lead to loss of the stored hydrogen, to blocking, or reduction of the storage volume of the porous storage [83].

Currently, the entire process analysis of the gas grid and its periphery is designed for hydrogen-free gas. Helium is used as carrier gas in gas chromatographic process analysis, and therefore hydrogen cannot be detected reliably at present. The use of other carrier gases (e.g., argon) is possible, but requires new authorization for the equipment [83].

Some end uses of natural gas use materials that are not suitable for high partial pressures of hydrogen, e.g., if decarburization of nonalloy ferritic steels occurs. Every single end use should therefore be checked for compatibility with higher concentrations of hydrogen.

Due to the different combustion characteristics of natural gas and hydrogen, the internal settings of large industrial burners, e.g., in the glass and steel industries must be changed. Since these are usually optimized to the desired application, a fluctuating gas composition leads to different thermal behavior and variations in product quality.

Even more critical are processes, especially in the chemical industry, in which natural gas is used as feedstock, in particular the steam reforming of natural gas. A fluctuating composition of the used gas leads to variation in the product gas ($CO:H_2$ ratio), which requires an additional adjustment depending on the subsequent use. Accordingly, for these processes, clarification and possibly significant adjustment are needed when running on natural gas with fluctuating composition.

To equip the natural gas grid for such higher hydrogen concentrations (up to 10 vol %), the transmission system operators (TSOs) assume adjustment costs of 3.73 billion € [84]. This does not include the resulting adjustment costs in the periphery and on the part of end users.

Unlike hydrogen, artificially produced methane is fully compatible with the existing natural gas infrastructure. Optionally, the heating value can be adjusted by blending with higher gaseous hydrocarbons.

Cavern Storage

In the natural-gas grid, storage caverns are used to offset diurnal fluctuations. At present, Germany has pore-storage facilities at 20 locations with a total of 260 caverns, a working volume of 14 315 million m^3 and a plateau-withdrawal rate of 484 million m^3d^{-1}. The storage caverns are operated commercially and are currently being greatly expanded. At 7 sites, a total of 82 caverns with a working gas volume of 3959 million m^3 are planned or under construction [10]. In principle, cavern storage facilities are suitable for storing natural gas with high hydrogen contents, synthetic methane, and hydrogen.

Pore Storage

In the gas grid pore-storage facilities are used for seasonal storage because of their slower gas uptake and release. Currently, Germany operates commercial pore-storage facilities at 20 locations with a working gas volume of 9 784 million m^3 and a plateau withdrawal rate of 170 million m^3d^{-1} [10]. The suitability of pore-storage facilities for the storage of hydrogen-containing gases is controversial. The high surface area of the pore-storage medium increases the risk that bacteria growing on the basis of hydrogen find ideal living conditions. In fact, past experience has shown a volume loss when storing hydrogen-rich gases [83]. Hence, it can currently be assumed that pore storage is not suitable for storing hydrogen-rich gases and pure hydrogen. In contrast, the storage of synthetic methane poses no problem.

4.2.7 Energy Storage in the Fuel Network

The fuel network with its various components (tanks, pipelines, ships, tankers) has a considerable internal storage capacity for liquid fuels, which is difficult to estimate. The main task of these components lies in the transportation and distribution of fuels, not in their storage.

Cavern Storage of Crude Oil, Petroleum Products, and Liquefied Petroleum Gas

According to the German *Erdölbevorratungsgesetz* (Petroleum Stockpiling Law) [9], operators are obliged to store a supply of 90 d of the net imports of petroleum products for times of crisis. In Germany, this is administered by the German national petroleum stockpiling agency, a corporation of public law. Storage can also take place outside Germany, in another member state of the EU. In the 2015/16 financial year, 23.6 million t of oil products were stored. Currently, 22.6 million t must be withheld to comply with legal requirements [85]. Currently, a total of 103 storage facilities are operated at 12 locations [10]. Expansion to nine additional caverns is planned or being implemented.

4.2.8 Options for the Use of Chemical Energy Storage

Industrial Value Chains Based on Hydrogen

Currently, hydrogen is used mainly in the chemical and petrochemical industries, and to a lesser extent in the glass and metals industries. Hydrogen currently plays no role as a fuel. Fig. 23 illustrates the current usage paths of hydrogen. In the metallurgical industry hydrogen-rich associated gases may be generated as part of the smelting process, which can be exploited thermally to decrease the fuel consumption. The large-scale production of hydrogen by means of renewable energy allows entry into a variety of industrial and energy-sector-specific value chains. In many cases, conversion to other substances is necessary or advantageous in order to use existing structures. An overview of the industrial and energy uses is shown in Fig. 24.

Refineries

Refineries produce the required hydrogen mainly by catalytic reforming, with the aim of improving the antiknock properties of the fuel product. Additional needs are covered by the gasification of vacuum distillation residues. Hydrogen is already used today as an important feedstock in refinery processes and in large quantities for the desulfurization of crude oil. This process will gain importance in the future because the quality of the crude oil will become progressively worse and the sulfur content will tend to increase. In principle, hydrogen is also suitable for increasing the fraction of usable components (i.e., those that have a relatively high H:C ratio) in crude oil and thus to increase the yield of a refinery. However, the cost specifications place high demands on the lowest possible price of hydrogen. Furthermore, significant additional quantities would be needed for large-scale use of hydrogen in the refinery sector.

Chemical Industry

Hydrogen is used in large amounts in the chemical industry. The production of hydrogen by electrolysis is thereby the exception and is used only when small amounts are needed. The most important process for hydrogen production is the steam reforming of natural gas, which leads to a hydrogen-rich synthesis gas, the processing of which depends on the downstream

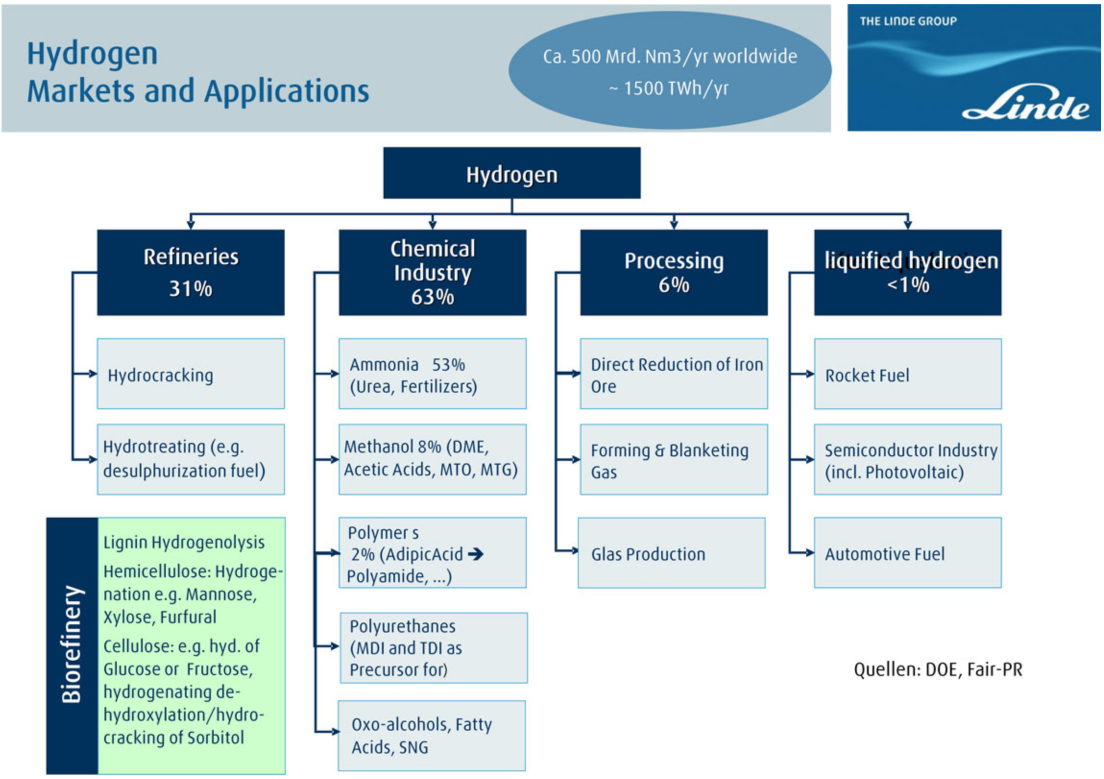


Figure 23. Current value chains of hydrogen; © Linde AG [86].

processes. Besides natural gas, other carbon-containing fuels, such as coal, oil, biomass, and waste, are used. Other sources of hydrogen are coupled streams from other processes, e.g., from the chlor-alkali electrolysis and dehydrogenation reactions. Regeneratively produced hydrogen is available by electrolysis using regeneratively produced electricity (water, solar, wind power) and an interesting option to convert excess power into valuable compounds.

The chemical industry uses large quantities of hydrogen for the production of ammonia. This process consumes about half of the total hydrogen produced worldwide. Modern ammonia plants are highly integrated and optimized. Potential for future development is expected for the use in biorefineries since generally the excess oxygen-containing functional groups of biogenic raw materials must be removed.

Another important process using large amounts of hydrogen is the production of methanol from synthesis gas:

$$\mathrm{CO} + 2\,\mathrm{H_2} \rightarrow \mathrm{CH_3OH},$$
$$\Delta H_{\mathrm{R}}^{0} = -128\ \mathrm{kJ\,mol^{-1}}$$

Methanol has considerable potential as feedstock for the production of organic raw materials by substituting petrochemical processes (e.g., to produce propylene, olefins, aromatics, and their numerous derivatives) through methanol-to-propylene (MTP), methanol-to-aromatics (MTA), and methanol-to-olefins (MTO) processes. Conventional catalytic processes can convert these olefins to short- to medium-chain hy-

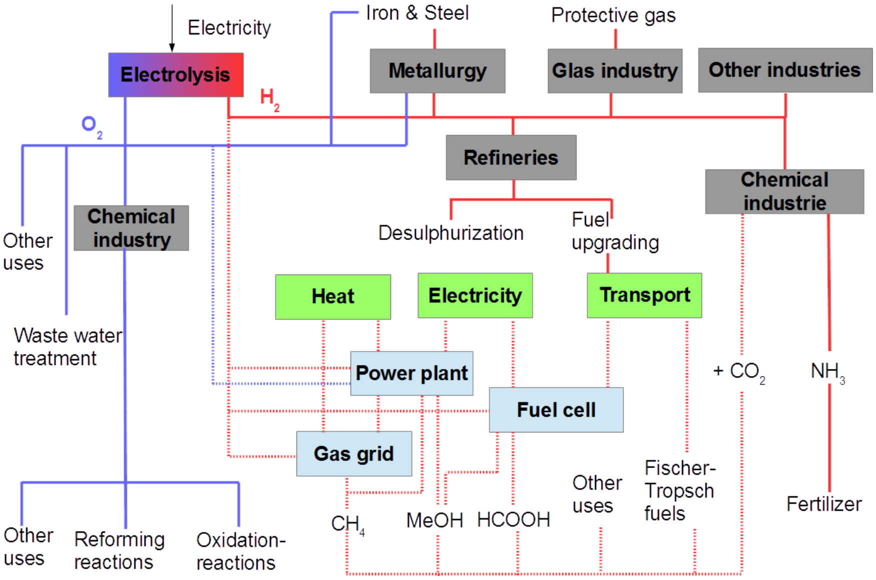


Figure 24. Potential energy and industrial value chains for electrolytically produced hydrogen.

drocarbons. Fig. 25 shows the value chains starting from methanol.

If renewably produced hydrogen becomes available in the future in sufficient quantities or in small production volumes at certain locations with a large local supply of surplus power, the production of methanol from CO_2 as carbon source via the generation of synthesis gas by means of dry reforming or by a selective direct hydrogenation could be an attractive option.

In principle, the production of formic acid can also be realized through a catalytic process based on hydrogen [87]:

$$CO_2 + H_2 \rightleftharpoons HCOOH, \quad \Delta H_R^0 = -31\ \mathrm{kJ\ mol^{-1}}$$

Compared to the classical route via the carbonylation of methanol with subsequent hydrolysis of the formate, this may be attractive for smaller production volumes at certain locations with large local supply of surplus electricity.

The synthesis of ammonia will remain the dominant hydrogen-based process for the foreseeable future. However, additional, electrolytically generated hydrogen could, together with its coproduct oxygen, be the reducing or oxidizing agent for chemical processes on a larger scale than is currently the case.

Metallurgy

There have been efforts in the past to replace coke as an essential reducing agent in steel production. For this purpose, the use of hydrogen was also investigated. However, in the classical blast furnace process coke also has mechanical functions that cannot be taken over by a gas. The Circored® process uses hydrogen as a direct reducing agent in the fluidized bed and was industrially implemented in Trinidad with an annual production of 500 000 t a^{-1} of hot briquetted iron (HBI) [88]. Currently, the plant is owned by Acelor Mittal and is not in operation. A change of global steel production to hydrogen as a reducing agent would create a demand of around 52 million t of hydrogen, approximately equaling today's global hydrogen production. In Europe, 5.8 million t of hydrogen would then be required for steel production [89]. In 2012, European hydrogen production was 4.8 million t a^{-1}. Currently, hydrogen is not competitive with other reducing agents (coke and electricity). Hydrogen is also used in the surface treatment of metals for specific applications, especially for semiconductors. For this application, high-purity hydrogen from electrolysis processes is used.

Energetic Use of Chemical Energy Storage

For energy use, direct reconversion via stationary fuel cells, combustion in modified gas turbines, or use in gas-and-steam power plants (combined-cycle power plants, CCPP) is possible. Oxygen could also be used for combustion in order to reach higher temperatures and higher efficiencies than in the current state of the art power plants. Thus, positive balancing energy and possibly heat is provided. This usage is, however, in direct cost competition with the use of fossil natural gas in gas turbines and CCPPs.

Stationary Usage

Modern power plants can use hydrogen, methane, and methanol in in the same manner as conventional fossil fuels. Particularly methane, as the main component of natural gas, is unproblematic in this respect. Fluctuating hydrogen contents in the fuel of gas turbines lead to instability in the flame geometry, unsteady flame propagation, and even flame extinction [61]. Therefore, the turbine manufacturers are cautious in their assessment of the use of hydrogen-rich gases. Methanol, however, can be fed without problems, but due to its lower energy density it leads to changes in the combustion behavior in comparison with conventional fuels, which must be taken into account. Currently, modern CCPPs reach an electrical efficiency of 60 %. In principle, the use of cogeneration plants is desirable to achieve the highest possible overall efficiency.

Water electrolysis as a key technology of material energy storage also produces a considerable amount of oxygen in addition to hydrogen. In thermal processes, combustion in pure oxygen or enrichment of atmospheric oxygen could be contemplated. Thus, higher combustion temperatures and improved efficiency of the power plants could be realized. However, this is expected to also lead to increased material specifications associated with a change in the combustion characteristics and would therefore have to be examined specifically.

In fuel cells, hydrogen and oxygen are combined in a reverse electrolysis. Thereby, electric current is formed and can be delivered to the grid. Analogous to electrolysis, different variants exist, whereby especially the PEM fuel cell in the low-temperature range (< 100 °C) and the solid-oxide fuel cell (SOFC) at high temperatures (> 600 °C) are considered promising. Furthermore, fuel

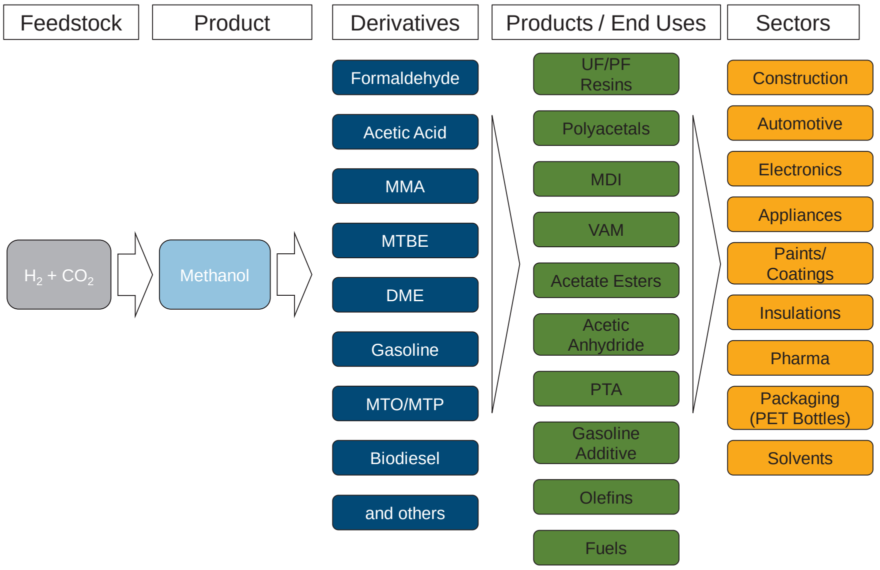


Figure 25. Value chains in the chemical industry, starting from methanol.

cell systems exist that can be operated with alternative fuels, such as the direct methanol fuel cell supplied with pure methanol [90].

Fuel cells achieve electrical efficiencies of up to 60 %. In stationary applications, they are mainly used in cogeneration of heat and power. The advantage of the fuel cell is its compactness. Similar to the redox flow battery, the converter, i.e., the fuel cell, and the storage are separated and therefore can be dimensioned freely with respect to storage and reconversion performance. However, as of now there is no long-term experience with the use of fuel cells as large-scale producers in the electricity system.

Besides centralized use, energy storage materials can also be used in local and mobile structures. However, this presupposes the existence of a functioning transport infrastructure. Also, chemical energy storage via, e.g., fuel cells, can be used for off-grid power supply and for emergency power supply of hospitals and other consumers where electricity supply must not fail.

Chemical Energy Storage and Mobility

Chemical energy storage can be used for mobile applications. FT fuels are directly designed for this application and can replace hydrocarbon fuels. Methanol can be added to existing fuels. In both cases, the existing mobility infrastructure can be used without further changes, that is, without substantial additional costs. Methane can also be used in natural gas vehicles, which are far less numerous, without further changes.

The number of passenger cars in Germany is, according to the *Kraftfahrtbundesamt* (Federal Motor Transport Authority), nearly 45.1 million, of which 556 000 are powered by natural gas or liquefied petroleum gas (1.3 %). Electric and hybrid vehicles amount to around 155 000 registered units [91] (2016). Fuel-cell-powered vehicles are at present not included in the statistics. It is assumed that worldwide 500 cars and 100 buses are supplied by more than 200 hydrogen fueling stations [92].

Hydrogen is introduced into the mobility sector via fuel-cell-powered vehicles. These vehicles are characterized by a much higher efficiency than conventional vehicles driven by internal combustion engines. For example, the consumption of the Mercedes-Benz B-Class F-Cell is around 1 kg_{H2}/100 km, which corresponds to approximately the equivalent of approx. 3.3 L diesel/100 km [93]. All major car manufacturers have significant R&D programs with the aim of developing production-ready fuel-cell-powered vehicles. Hyundai has already entered small-series production with the ix35, and Toyota has entered the market with its mass-produced Mirai model in 2015.

The use of vehicles powered by fuel cells or batteries partly integrates private motor vehicles into the European Emissions Trading Scheme (ETS), since the electricity sector is recognized by the ETS. Thus, the cap on total emissions in the ETS region would also cover this part of the mobility sector and contribute to the reduction of CO_2 emissions. Currently, conventional diesel- or gasoline-driven private transport is not covered and its emissions are in addition to those of the electricity sector.

For an area-wide supply of vehicles with hydrogen, significant investments must be made in the infrastructure. The price of fuel-cell-powered vehicles in the foreseeable future is significantly higher than that of cars with conventional drive technology. However, it is expected that the price of hydrogen from renewable sources at the gas station will be similar to those of current conventional fuels (see also the calculation example in Sect. 5.2).

4.2.9 Use of Co-products of Hydrogen Production

Oxygen

In the production of hydrogen by electrolysis of water 8 t of oxygen is formed stoichiometrically for 1 t of hydrogen. The use of surplus electricity to produce hydrogen would produce oxygen in quantities that go far beyond the current uses. This can be seen as an opportunity. In principle, pure oxygen can be used for combustion processes instead of air. The chemical and metallurgical industries already use oxygen for oxidation reactions.

In the steel industry, new concepts are being developed that increasingly work with pure oxygen instead of air [94], with the aim of increased CO_2 concentrations in the exhaust gas that are better suited for separation. Similarly, the cement industry has developed processes that use oxygen-enriched gas. A pilot plant using oxygen-enriched air in the precalcination stage has been operated in Denmark [95].

Sewage treatment plants use oxygen to process carbon- and nitrogen-containing wastewater. A wastewater treatment plant for the supply of a settlement of 20 000 inhabitants requires approximately 3.3 t d^{-1} of oxygen, which, in the case of delivery via electrolysis, is associated with a combined production of approximately 413 kg d^{-1} of hydrogen. Industrial wastewater treatment plants have very specific wastewater loads and accordingly widely varying oxygen demand. The pulp and paper industry is also characterized by a very high oxygen requirement for the processing of wastewater loads. Therefore, synergies could result from the use of oxygen, which will improve the efficiency of water electrolysis. However, large amounts of oxygen are presently produced by air separation already. It is unlikely that oxygen as a coproduct of water electrolysis will be economically competitive. The technical handling of pure oxygen is demanding and places high demands on safety precautions.

It should also be considered whether the oxygen content in air for the combustion of fossil fuels in power plants can be increased in order to achieve higher combustion temperatures and improved efficiencies.

At present, discussions revolve almost exclusively around water electrolysis to produce hydrogen for storing electrical energy, whereby oxygen is obtained at the anode. In principle, however, other anode reactions seem possible to make production of valuable resources more economical. An industrially used reaction is the chlor-alkali electrolysis, in which the hydrogen formed at the cathode is not the target product, but the anodic chlorine. Here, the targeted examination of other possible electrochemical reactions could open up new options that provide controlled energy, form hydrogen as an energy storage material, and generate another product of value at the anode.

Heat

Besides oxygen, a considerable amount of heat is produced during the electrolysis of water, albeit at quite a low temperature ($T < 100\,°C$). The efficiency of the electrolysis may benefit from a local heat consumer operating on the corresponding temperature level (e.g., in the food industry).

4.2.10 Advantages of Chemical Energy Storage

The conversion of chemical energy storage to other usable forms of energy is either done by combustion in a power plant or by cold combustion in a fuel-cell system. Chemical energy storage materials have higher energy densities than electrochemical, mechanical, or thermal storage and can store large amounts of energy in a very compact form.

In principle, power-to-X processes are able to provide negative balancing energy for the electricity grid, where X stands for any product. Power-to-gas (PTG) describes the conversion of electricity to gaseous products (hydrogen, methane), power-to-liquid (PTL) the conversion of electricity to liquid products, power-to-fuel the conversion of electricity to fuels, power-to-heat (PTH) the conversion of electricity to heat, power-to-X the conversion of electricity to other products/compounds, and power-to-chemicals (PTC) the conversion of electricity to products that can be integrated into the value chains of the chemical industry.

The key technology hereby is water electrolysis, which can be designed to be sufficiently dynamic for buffering of peak performance. Thereafter, the various process chains can convert the hydrogen to different fuels and thus address the energy needs in various fields of use as well as exploit the specific advantages or the storage capacity of the natural gas grid. The refined fuels often have their own industrial value chains.

This procedure can in principle reduce the dependence of the industry on imports of fossil fuels. New value chains could be formed by a shift in the raw materials base. If the secondary conversions are carried out with CO_2 from biogenic sources, climate-neutral fuels and industrial raw materials can contribute to the sustainability of the corresponding sectors. Optionally, CO_2 allowances can be claimed for accumulating substances. However, this is not provided for in the current regulations of the ETS. A variable amount of energy could be stored in order to operate the subsequent process steps continuously. For example, the use of storage caverns for H_2 and CO_2 may allow continuous operation of downstream methanation/methanolation and FT processes.

Chemical energy storage materials can substitute conventional fuels in the transport sector and thus improve the greenhouse gas balance of the transport sector and reduce dependence on imported fossil fuels. Their use leads to increased cross-linking of the electricity and transport sectors (see also Sect. 4.6).

4.2.11 Disadvantages of Chemical Energy Storage

Providing positive balancing energy for the power grid requires capacities for reconversion to be maintained, e.g., combined cycle power plants, or the deliberately reduced operation of electrolyzers. The investment must then be profitable despite fewer operating hours.

The chemical energy storage compounds are always in economic competition with their conventionally produced counterparts in a given application. It is not currently anticipated that the storage materials can be manufactured at a competitive cost level compared to conventional products. Potentially flexible utilization pathways may thus remain blocked or require subsidies. An evaluation of various PTC routes by Siemens showed that the products are significantly more expensive than their fossil equivalents. Methanol fares the best, while the production of methane has the least favorable price in relation to fossil natural gas [96].

The result would be two different price levels for the same substance, i.e., the storage substance produced by PTC and the world market price of the conventional substance. This situation, which exists in a similar form for diesel fuel/heating oil and ethanol, can lead to misuse and therefore requires a critical evaluation and possibly regulation.

Tab. 7 compares the potential of various storage materials, indicating their world-scale plant size. Tab. 8 summarizes the state of PTC technologies. Considering a regionally unbalanced distribution of the surplus power and the fact that its supply fluctuates temporally, it will be difficult to guarantee production of methanol, ammonia, or FT fuels at reasonable cost

Table 7. Potential of various chemical energy storage options of surplus power.

Storage material	Reaction	Efficiency[a]	Current surplus power: 4.7 TWh a^{-1} (2015) [19]
Hydrogen	Water electrolysis: $H_2O \rightarrow H_2 + 0.5\ O_2$	Electrical – H_2 (LHV): 70 %; electrical – H_2 (HHV): 80 %	94 kt H_2 (4.5 kWh m^{-3} H_2)
Methane	Methanation: $4\ H_2 + CO_2 \rightarrow CH_4 + 2\ H_2O$	LHV: 83 %	186 kt CH_4
Methanol (plant size 1 million t a^{-1})	$3\ H_2 + CO_2 \rightarrow CH_3OH + H_2O$	LHV: 88 %	497 kt CH_3OH
Ammonia (plant size 0.5–1 million t a^{-1})	$3\ H_2 + 2\ N_2 \rightarrow 2\ NH_3$	LHV: 94 %; 90 % (with ASU[b], 243 kWh t^{-1} N_2)	528 kt NH_3
FT fuels (PLANT size > 1 million t a^{-1})	$(3n+1)\ H_2 + nCO_2 \rightarrow C_nH_{2n+2} + 2n\ H_2O$	LHV: 83 %	217 kt FT fuel

[a] The chemical energy conversions to other energy sources are indicated as comparisons of the lower calorific value of the products and the starting materials, as given by the stoichiometry; they therefore represent theoretical maximum values; [b] ASU = air separation unit.

Table 8. Storing energy in chemical energy storage.

Technology/ Parameter	Water electrolysis	Conversion to methane	Conversion to methanol	Conversion to ammonia	Reconversion CCGT methanol / CH_4/H_2	Reconversion with fuel cell	Conversion to higher hydrocarbons	
							FT	MTG
Performance range	MW	MW	MW	MW	MW	kW	MW	MW
Storage capacity	MWh	MWh	MWh	MWh	MWh			
Reaction time	min	Continuous operation	Continuous operation	Continuous operation	min	min	Continuous operation	Continuous operation
Plant life [a]	Alkali > 20; PEM, SOEC not known	> 20	> 20	> 20	> 20		> 20	> 20
Efficiency of conversion$^{a)}$ [%]	70 (76)	83 (theoretically, LHV)	88 (theoretically, LHV)	100$^{b)}$	60 (electricity) or 95 KWK	50 (electricity)	83 (theoretically, LHV)	
Specific energy density [$kWh\,kg^{-1}$]	33.3	13.9	5.5	5.2			≈11.9	12.1
Volumetric energy density (1 bar/30 bar) [$kWh\,L^{-1}$]	0.0027 (gas, 1.013 bar)/1.3 (gas, 700 bar)/ 2.4 (liquid)	0.0091 (gas, 1.013 bar)/ 0.27 (gas, 70 bar)	4.4 (liquid)	0.0036 (gas, 1.013 bar)/3.8 (liquid)			≈9.5 (liquid)	≈8.9 (liquid)
Investment costs power (system) [€ kW^{-1}]	~1000 (alkaline); ~2000 (PEM); ?? (SOEC)							
State of technology	Technical implementation (large scale)	Demonstration	Technical implementation (large scale)	Technical implementation (large scale)	Technical implementation (large scale)	Development	Technical implementation (large scale); research (small scale)	Technical implementation (large scale); research (small scale)
Notes	Discontinuous operation possible; reference price: H_2 steam reforming; industrial use (chemicals, refining, metallurgy, etc.)	CO_2 from biogas; methane is directly compatible with the natural gas grid	Biogenic and fossil CO_2, methanol can be used directly as fuel/chemical raw material		Modern CCPP, turbine materials not designed for H_2; for methanol conversion with ca. 3 million €/ turbine possible; 9 % more power generating efficiency compared with CH_4 [60]		CO_2 from biogas; feed into fuel and propellant networks possible; reference price: fuels and propellants	

a) Compare discussion in Sect. 3.2.; values refer to the net calorific value (lower heating value); b) combustion of $2\ NH_3 + 1.5\ O_2 \rightarrow N_2 + 3\ H_2O$.

structures, even assuming the availability of large quantities of cheap surplus electricity in 2032. However, the investment costs of these conventional systems are dominated by the production of synthesis gas, which would be significantly reduced with the use of electrolytically produced hydrogen. On the other hand, the costs of separation, purification, and delivery of CO_2 for its conversion would also have to be taken into account.

4.3 Technologies for Storage in the Form of Electrochemical Energy

Batteries are one of the established standard technologies for storing electrical energy by conversion into a chemical energy carrier via an electrochemical process. Charging and discharging should be reversible so that good storage efficiency and

Table 9. Overview of batteries.

Battery type	Cycles	Efficiency [%]	Battery costs [€ kWh^{-1}]	System costs [€ kWh^{-1}]	Development status
Lead-acid	300–2000	75–90	100	300–600	Technical implementation
Nickel-cadmium	1000	60–65	400		Technical implementation
Nickel-metal hydride	1400	70	550		Technical implementation
Lithium-ion	5000–15 000	90–95	300–500	1000–1500	Technical implementation (consumer goods), demonstration (stationary)
Sodium-sulfur (high-temperature battery)	3000–7000	70–85	100–200	130–230	Technical implementation
Zinc-air	4000 (target)	60–70	–	250–300	Development
Redox flow	20 000	70–85	–	500–650	Development

high cycle stability can be achieved. Other important properties are the energy density, power density, and the availability and cost of the materials used. The charged battery can provide consumers with electrical energy within a short time. Therefore, already today batteries serve, among others, as emergency uninterruptible power supplies (UPS) for computers, to bridge the period until the startup of emergency generators, and as starter batteries in cars, for which they are ideally suited. However, the chemical self-discharging of the battery, aging due to frequent charging and discharging, and the calendrical aging of structures and materials must be taken into account. Since usually the solid electrode materials are the chemical energy storage materials, the battery capacity is limited by the mass of the electrode materials, and the electrical power by the rates of the reactions. Hence, large, porous electrode surfaces are the key to achieving high power density. An exception are the redox flow batteries, which use dissolved salts for chemical energy storage so that their capacity can be varied by means of the size of the reservoir, regardless of the power rating of the electrochemical cell. For connection of the batteries to the power supply, voltage transformers are required. The currently discussed electrochemical energy storage systems for use in the power grid are summarized in Tab. 9. Since intermediate storage of electrical energy always leads to an efficiency loss and additional investment costs, a correspondingly large difference between the cost of the electrical energy to be stored and the released energy is required to make batteries economical.

4.3.1 Electrochemical Energy Storage

Lead-Acid Battery

The lead-acid battery is the most common electrochemical energy storage system. As car starter batteries about 70 million lead-acid batteries are produced each year in Europe, at a cost of about 100 € kWh^{-1} capacity. During discharge of the battery, metallic lead is oxidized to lead sulfate at the negative electrode, and lead dioxide is reduced to lead sulfate at the positive electrode. The open-circuit voltage per cell is 2,1 V, and the final discharge voltage is approximately 1.8 V. The charge voltage should not exceed 2.3–2.4 V, otherwise, water will be split into gaseous oxygen and hydrogen:

Negative pole (discharge): $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2\,e^-$

Positive pole (discharge): $PbO_2 + SO_4^{2-} + 4\,H_3O^+ + 2\,e^- \rightarrow PbSO_4 + 6\,H_2O$

Overall reaction: $Pb + PbO_2 + 2\,H_2SO_4 \rightarrow 2\,PbSO_4 + 2\,H_2O$

Because of their short lifetime and cycle stability – the battery starts losing capacity after 100 charging and discharging cycles – cheap starter batteries with liquid electrolytes are not suitable for stationary energy storage. Lead-acid batteries with higher cycle stability, in which the sulfuric acid is fixed in gels or glass fiber fleece, already cost 200 to 300 € kWh^{-1} and have been the state of the art in stationary battery applications for decades. Lead-acid batteries for storage of domestic solar power are also often oversized by a factor of two in order to obtain acceptable service lifetimes of approximately ten years with a total of 2000 cycles. Complete systems for solar energy storage in a family house, including lead-acid battery, battery transformer, PV production meter, and bidirectional meter, cost more than 1000 € kWh^{-1}.

Nickel-Metal Hydride Batteries

Nickel-metal hydride batteries have been developed as improvement to nickel-cadmium batteries. Instead of the toxic heavy metal cadmium, its negative electrode is made of a metal alloy consisting of lanthanum, cerium, neodymium, and nickel, which can absorb hydrogen to form a metal hydride (MH). The metal hydride is capable of undergoing reversible hydrogen absorbing-desorbing reactions as the battery is charged and discharged. During discharge the metal hydride is oxidized to the metal (M) and a proton. The protons react with the hydroxide ions of the potassium hydroxide solution to form water. At the positive electrode, trivalent nickel oxide hydrate is reduced to bivalent nickel hydroxide:

Negative (discharge): $2\ \mathrm{MH} + \mathrm{OH}^- \rightarrow \mathrm{M} + \mathrm{H_2O} + \mathrm{e}^-$

Positive (discharge): $\mathrm{NiOOH} + \mathrm{H_2O} + \mathrm{e}^- \rightarrow \mathrm{Ni(OH)_2} + \mathrm{OH}^-$

Overall reaction: $\mathrm{MH} + \mathrm{NiO(OH)} \rightarrow \mathrm{M} + \mathrm{Ni(OH)_2}$

NiMH single cells are enclosed in a steel container which is equipped with a pressure-relief valve. The working voltage is 1.2 to 1.3 V. They can be operated from –20 to +60 °C.

In the automotive sector NiMH batteries have proven their suitability in more than 15 years of mass production. They are, e.g., utilized in the full hybrid vehicle Toyota Prius and are equally suitable for large stationary systems for emergency power supply and uninterruptible power supply. In 2004, the American company Cobasys developed a NiMH system for uninterrupted power supply which can provide a power output of 560 kW for 15 min. The battery system consists of 48 modules with a capacity of 85 Ah each.

Lithium-Ion Batteries

Mobile phones, cameras, and other portable devices are powered by lithium-ion batteries, which are produced almost exclusively in Asia. Lithium batteries are considered the front runners in the competition for mobile and stationary battery systems on market. They are voltage-stable and suitable for fast charging. They also have a high energy density of up to 200 Wh kg^{-1} and high cycle stability, and can therefore be frequently charged and discharged.

During discharge, the lithium, which is embedded in graphite or titanium oxide in the negative electrode, is oxidized to lithium cations, while at the positive pole a transition metal oxide is reduced, so that it can intercalate lithium ions. In the charging and discharging cycles lithium ions migrate back and forth between the electrodes, which are 40–90 µm thick. The following reaction equations show the processes for graphite anodes and lithium cobalt oxide cathodes during discharge in detail ($x \approx 0.5$):

Negative (discharge): $\mathrm{Li}_x\mathrm{C_6} \rightarrow \mathrm{C_6} + x\ \mathrm{Li}^+ + x\ \mathrm{e}^-$

Positive (discharge): $\mathrm{Li}_{1-x}\mathrm{CoO_2} + x\ \mathrm{e}^- + x\ \mathrm{Li}^+ \rightarrow \mathrm{LiCoO_2}$

Overall reaction: $\mathrm{Li}_x\mathrm{C_6} + \mathrm{Li}_{1-x}\mathrm{CoO_2} \rightarrow \mathrm{C_6} + \mathrm{LiCoO_2}$

The electrolyte between the electrodes must be able to conduct lithium ions. To prevent direct electrical contact of the electrodes, a porous separator is used, which is impregnated with an organic electrolyte and provides an important safety feature. Because lithium reacts violently with water, lithium-ion batteries must be completely anhydrous.

With respect to the materials for the positive electrode, the possibilities are numerous. Mostly oxides or phosphates of iron, nickel, manganese, aluminum and cobalt are used, which are stable in different oxidation states and can insert lithium ions during discharge. As the negative electrode, graphite or lithium titanium oxide are often used. By combining the different electrode materials open-circuit voltages of 2–5 V can be achieved.

Lithium-ion batteries require a battery management system that monitors the key operational parameters during charging and discharging such as voltages and currents as well as the battery temperature. Because of the abundance of material combinations, their future development potential is considered to be very high. Current research deals with lithium-air and lithium-sulfur batteries, in which metallic lithium is used as the negative electrode. They could potentially achieve a much higher energy density: lithium-air batteries have a theoretical energy density of approximately 11 kWh kg^{-1} (at 3.0 V), and lithium-sulfur batteries of 2.5 kWh kg^{-1} (at 2.1 V).

Lithium-ion batteries for small electronic appliances are state of the art. Their use as a stationary bulk storage is currently being tested in Schwerin. Tesla announced the construction of a gigafactory to benefit from the economy of scale in the production of Li-ion cells. Full production output is expected in 2018 [97].

Lithium-Sulfur Batteries

The lithium-sulfur battery is currently the subject of intense research. The advantages of a potentially very high energy density (theoretically up to 2.5 kWh kg^{-1}, currently 600 Wh kg^{-1} [98] are reached) and readily available, inexpensive sulfur as a cathode material make this battery interesting for the automobile applications.

The electrochemical discharge reaction of the cell is:

$2\ \mathrm{Li} + 1/8\ \mathrm{S_8} \rightarrow \mathrm{Li_2S}$

The company Sion Power, USA, has been a pioneer in the development of this battery, now in cooperation with BASF AG.

Sodium-Sulfur Batteries

The sodium-sulfur battery, the technical principles of which were developed in the early 1980s, is a high-temperature battery. It operates at 300–350 °C. Sodium-sulfur batteries have a cylindrical configuration: Inside is the molten sodium electrode, which is enclosed in a metal container for safety reasons. A sodium-ion-conducting ceramic constitutes the solid electrolyte. It is the centerpiece of the battery, which is surrounded by a molten-sulfur electrode. During discharge, sodium is oxidized at the negative electrode and sulfur is reduced at the positive electrode. Thereby, various sodium polysulfides are formed ($\mathrm{Na_2S}_x$, x = 3–5). The open-circuit voltage of a charged sodium-sulfur cell is 2.07 V:

Negative (discharge): $2\ \mathrm{Na} \rightarrow 2\ \mathrm{Na}^+ + 2\ \mathrm{e}^-$

Positive (discharge): $x\ \mathrm{S} + 2\ \mathrm{e}^- \rightarrow \mathrm{S}_x^{2-}$

Overall reaction: $2\ \mathrm{Na} + x\ \mathrm{S} \rightarrow \mathrm{Na_2S}_x$

Sodium–sulfur batteries are sold exclusively by NGK Insulators. A typical battery module has an electrical power of 50 kW and a capacity of 300 kWh. The modules consist of cylindrical cells, the interstices of which are filled with sand. The efficiency of sodium-sulfur cells is 80–85 %.

From these 50-kW modules larger battery systems are built, which have a capacity of several MWh. The Kyusyu Electric Power Co.,Inc. operates a battery system with 50 MW power and 300 MWh capacity to stabilize solar power [99]. Another major energy storage facility based on sodium-sulfur batteries is located in Presidio, Texas. It is used to compensate for voltage fluctuations in the grid and as an emergency power supply. With an output of 4 MW it can store 32 MWh of electricity. The capital expenditure for the total system is reported to be 25 Mio. USD. [100].

The lifetime of a sodium-sulfur battery is around 15 years. However, the depth of discharge affects the number of cycles. At 65 % discharge 7000 cycles are possible, but at the maximum discharge of 100 % only 2500 cycles.

Zebra Battery

A second variant of the high-temperature battery is the so-called Zebra battery, which is also based on liquid sodium as energy carrier. The electrochemical discharge reaction is as follows:

$$2\ \mathrm{Na} + \mathrm{NiCl_2} \rightarrow 2\ \mathrm{NaCl} + \mathrm{Ni}$$

Fiamm SoNick is selling Zebra batteries for stationary storage, whereas General Electric has stopped its activities in 2014.

Zinc–Air Batteries

Rechargeable zinc-air batteries are interesting for large-scale stationary energy storage, mainly due to the high energy content of zinc (about 1200 Wh kg^{-1} at 1.45 V). Also advantageous are the low material cost and environmental friendliness of zinc, which is almost completely recyclable. In addition, zinc-air energy storage devices are relatively safe to handle. Stationary zinc-air batteries with a capacity of 40 GWh, which corresponds to that of Germany's installed pumped-storage power plants, require about 100 000 t of zinc, equivalent to 1 % of the annual global zinc output. Unlike lithium, zinc is readily available.

During discharge, zinc is oxidized to zinc hydroxide in an alkaline electrolyte at the negative electrode, which precipitates as zinc oxide at supersaturation:

Negative (discharge):	$\mathrm{Zn} + 4\ \mathrm{OH^-} \rightarrow \mathrm{Zn(OH)_4^{2-}} + 2\ \mathrm{e^-}$
	$\mathrm{Zn(OH)_4^{2-}} \rightarrow \mathrm{ZnO} + \mathrm{H_2O} + 2\ \mathrm{OH^-}$
Positive (discharge):	$0.5\ \mathrm{O_2} + \mathrm{H_2O} + 2\ \mathrm{e^-} \rightarrow 2\ \mathrm{OH^-}$
Overall reaction:	$\mathrm{Zn} + 1/2\ \mathrm{O_2} \rightarrow \mathrm{ZnO}$

The theoretical open circuit voltage is 1.67 V; in practice, about 1.45 V is achieved. The operating voltage is between 1.0 and 1.2 V. For technical applications the cells could achieve efficiencies between 60 and 70 %.

Rechargeable zinc-air batteries are still in the research and development stage, since their cycle stability is still too low. The surface of the zinc plate electrodes changes too much during repeated charging and discharging. A possible solution is to pump zinc slurry, i.e., a suspension of zinc particles in an alkaline electrolyte, through the cell. The contact with a current collector makes the electron transfer during charging and discharging possible. On the other hand, in the development of reversible oxygen electrodes the focus lies on catalysts that are sufficiently active and stable both for oxygen reduction and oxygen evolution. Zinc-air batteries are not yet commercially available as rechargeable systems while primary batteries have long been on the market.

Redox Flow Batteries

Redox flow batteries are particularly well suited for stationary long-term storage of energy. In these batteries, the liquid energy carriers are stored in two tanks and are pumped through an electrochemical cell. In the cell, ion exchange is carried out by an ion-conducting membrane, which at the same time separates the two electrolytes. Electrodes are made of graphite-based composites. Since the 1960s, a number of redox pairs (iron/chromium, zinc/bromine, vanadium/bromine) have been tested for their suitability in redox flow batteries. The most advanced in terms of commercialization is the vanadium redox flow battery (VRFB), wherein on both sides of the cell dissolved vanadium salts are used in sulfuric acid. During discharge, vanadium(II) is oxidized to vanadium(III) at the negative electrode. At the same time, vanadium(V) oxide ions are reduced to vanadium(IV) oxide ions at the positive electrode:

Negative (discharge):	$\mathrm{V^{2+}} \rightarrow \mathrm{V^{3+}} + \mathrm{e^-}$
Positive (discharge):	$\mathrm{VO_2^+} + 2\ \mathrm{H^+} + \mathrm{e^-} \rightarrow \mathrm{VO^{2+}} + \mathrm{H_2O}$
Overall reaction:	$\mathrm{V^{2+}} + \mathrm{VO_2^+} + 2\ \mathrm{H^+} \rightarrow \mathrm{V^{3+}} + \mathrm{VO^{2+}} + \mathrm{H_2O}$

By separating the energy-converting battery cell from the energy-storing electrolyte tanks, the power and stored energy can be scaled independently. Redox flow batteries achieve efficiencies of up to 80 %, negligible self-discharge (< 1 % per annum), and a high lifetime of 20 000 cycles. However, they operate only between 10 and 30 ° C, since above 40 °C, the pentavalent vanadium ions are irreversibly converted to solid vanadium oxide. Redox flow batteries also have relatively low energy densities, because the solubility of the vanadium ions in the electrolyte liquid is limited. A commercial VRFB storage unit with 100 kWh capacity weighs 10 t and has a volume of about 24 m^3. This corresponds to an energy density of 9.7 Wh kg^{-1}.

Those systems already studied in the 1980s, e.g., hydrogen-bromine and zinc-bromine, are again being regarded as promising candidates for redox systems. The hydrogen and bromine electrodes show excellent reversible behavior, and the energy densities are significantly higher than those of vanadium solutions. A combination of a bromine electrode with an organic electrode based on the redox process of anthraquinone/anthrahydroquinone is also promising and good results were already achieved [101]. The authors describe the favorable energy densities and costs of this new battery type compared with the vanadium battery. However, bromine is toxic and corrosive. A challenge for redox flow batteries is choosing the right scale-up strategy. A numbering-up will only be useful if the amount of maintenance can be kept within limits.

4.3.2 Electromobility as Decentralized Energy Storage

In principle, a fleet of battery-powered electric vehicles could be used for decentralized energy storage. With a fleet of approximately 1 million electric vehicles with a capacity of 20 kWh per vehicle, a storage capacity of 20 GWh would theoretically be available, although this would correspond to the full charging/discharging of the entire vehicle fleet. Since only vehicles that are connected to the power grid at a desired point in time and whose load state allows partial charging and/or discharging can be used, it can be assumed that the usable storage capacity comprises only a small fraction of the nominal capacity. In all these considerations, however, it must be borne in mind that the car user primarily has the mobility function of the car in mind. An effective energy management would require a major intervention in the mobility behavior of the user.

The current penetration of the car market with electric vehicles is very low (25 502 cars as of January 01, 2016 [91] in Germany). Under these circumstances, the expansion plan of the German National Platform for Electric Mobility [102], with the objective of bringing one million electric vehicles onto the roads by 2020, can only be described as extremely ambitious. Existing homogeneous commercial vehicle fleets, such as bus fleets of transport companies, consist of heavily used vehicles and are consequently only available for load management for relatively short periods of time.

Greater penetration of the car market opens up greater opportunities, because the average car in Germany is used only for about one hour per day. It is likely that time-controlled loading by an energy management system would find more user acceptance than controlled discharge, which directly limits the possibilities of use. A contribution to negative balancing energy is conceivable if, e.g., the loading takes place at night or at midday. Currently, no significant contribution of electric vehicles to grid stabilization is assumed, neither in the medium nor in the long term.

4.3.3 Advantages of Electrochemical Storage

Electrochemical storage systems are characterized by an excellent response time and thus can effectively compensate for short-term fluctuations. They can provide positive and negative balancing energy with high electrical efficiency and are used to store energy for mobile, off-grid, and emergency applications.

4.3.4 Disadvantages of Electrochemical Storage

Electrochemical storage systems are limited in their application range by their relatively low energy and power densities. Furthermore, both the calendrical and the cycle life of the systems are limited. Independent scaling of power and capacity is generally not possible, and this must be taken into account in the design. The battery costs rise in proportion to the capacity to be installed, at least above a certain size, so that economies of scale are only achieved concerning the system periphery. For large batteries, the cost for the electrical and electronic peripherals is approximately 10 %. For redox flow batteries, however, the storage capacity can be scaled independently of the power, so that the costs in case of high capacities increase proportionally to the costs of the liquid energy carriers (e.g., vanadium salt solutions). So far, there is no reliable information about lifetime from the ongoing operations. Tab. 9 provides an overview of the most common battery systems [103].

4.3.5 Operating Experience with Large-Scale Electrochemical Energy Storage

In the past, large battery storage facilities have hitherto been used only sporadically, e.g., lead-acid batteries with 17 MW/14.4 MWh in the isolated network BEWAG in West Berlin between 1984 and 1994. Other large-scale battery storage facilities based on lead-acid batteries have been installed and used in several countries [22]. Sodium-sulfur batteries from NGK [104] with up to 34 MW output have been installed in combination with a wind farm. Li-ion batteries, e.g., are used on the island of Pellworm with an output of 560 kW and a capacity of 1.1 MWh. In Schwerin, a large energy storage facility based on Li-ion batteries has been connected to the grid. The plant has a capacity of 5 MWh and an output of 5 MW. In the short term even 50 MW is possible. The battery manufacturer Samsung guarantees a lifetime of 20 years. The system did cost 6 million €, i.e., 1200 € kWh^{-1}. The installation was strongly supported by public funding [105]. Currently however, the storage of electricity on a large scale is still uneconomical, since the previously high price peaks at midday are capped by solar energy, so that even pumped hydro storage plants are struggling with low hours of operation. However, the global storage market for stationary batteries is growing fast. According to the London based research institute Global Data in 2016 around 1500 MW of battery energy storage systems were installed worldwide. Until 2020, the installed battery power is expected to grow almost tenfold to 14 000 MW [106].

4.3.6 Battery Systems for Solar Energy Storage

In recent years, a market for small, stationary battery storage has developed. Various manufacturers have commercialized so-called solar energy storage systems with approximately 5 kWh storage capacity. The built-in batteries are either lead-acid or Li-ion batteries. Although employing such storage systems in private households is currently not economically viable, a market is developing.

Current costs of the systems are not dominated by the batteries, but by the electrical/electronic components. For example, in 2014, a 5-kWh solar energy storage system costs between 7000 € with a lead-acid battery and 11 500 € with an

Li-ion battery. Since then prices, especially for Li-ion systems, have decreased significantly. A recent overview of available system can be found in [107]. Currently, these systems are supported by investment subsidies.

For large amounts of energy or extremely high performance, batteries are basically ill-suited as the investment costs are too high. In the energy range of GWh or TWh, hydrogen as chemical energy carrier offers the possibility to realize such large capacities, and the associated performance (a capacity of 10 GWh in 24 h corresponds to an electric power of 416 MW) can only be provided by gas turbines according to the current state of the art. In a VDE study from 2008, the costs for electricity from batteries in load-leveling operations are given for the different types of batteries in the range of 13–43 ct kWh^{-1}. In comparison, those of pumped-storage hydroelectric power plants lie between 3 and 5 ct kWh^{-1} [22].

4.4 Technologies for Energy Storage in the Form of Thermal Energy

The conversion of electrical energy to thermal energy is virtually lossless. Additionally, resistance heaters are relatively inexpensive. Thermal energy can be stored in thermal storage units to compensate, e.g., circadian variations in solar thermal power plants. Even seasonal storage is possible. District heating and steam systems can be used for short-term storage. Municipal heating networks are seasonal in use and are supplied by combined heat and power systems or cogeneration plants. Industrial steam networks, e.g., in industrial parks, are constantly in use. Denmark already uses its heat networks for storing excess electricity from wind farms [108]. An interesting possibility provided by thermal storage is heat transformation, i.e., discharge is carried out on a different (higher) temperature level than charging. Thereby, applications for higher temperature levels can be developed. Fig. 26 shows plots of performance versus capacity for various thermal energy storage systems, and Fig. 27 shows their frequency of use.

4.4.1 Water and Steam Storage

In the low-temperature range (< 100 °C) mainly liquid water is used as heat-storage and heat-transfer medium. Liquid water combines several positive characteristics: It has a high heat capacity, forms a stable vertical layer structure, which significantly reduces heat losses during storage, it is convenient, available, nonpolluting, and has no additional requirements for safe operation. Hot-water tanks are used in both private and commercial buildings. In addition to the installation of a storage tank in the building, also ground-water-containing layers, so-called aquifers [109], can be used as additional storage capacity. For higher temperatures, steam is used as heat-transfer medium. Depending on the pressure level, temperatures up to 300 °C can be used. Hot steam can be used stored in a so-called

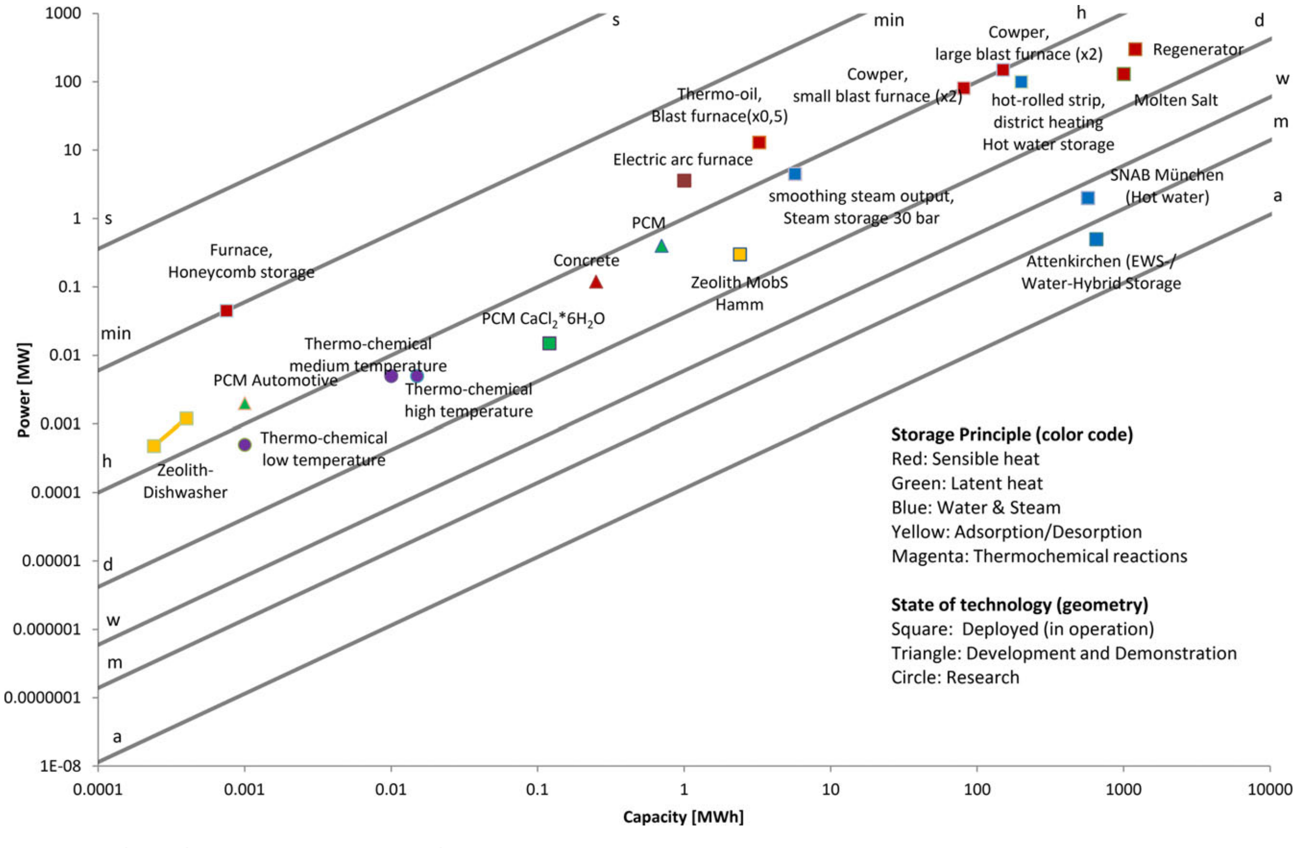


Figure 26. Thermal storage properties [110], shown as power versus capacity.

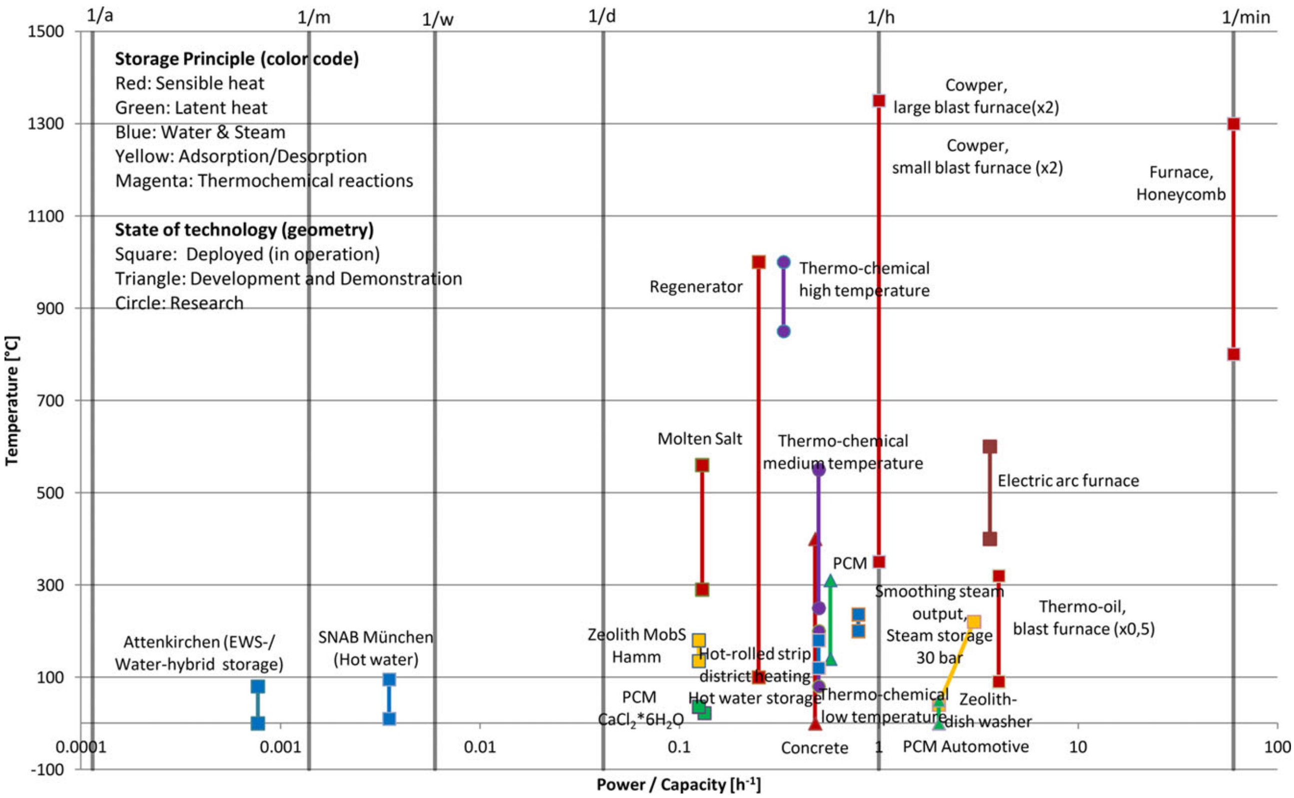


Figure 27. Overview thermal storage [110] as a function of the frequency.

Ruths steam accumulator and thus become available for later use. Water and steam accumulators can be easily integrated into the existing infrastructure.

Steam accumulators can be used in mobile applications, albeit to a very limited extent. In the past, many sites in the chemical industry applied steam accumulator locomotives in hazardous areas to reduce the risk of explosions. The boiler of the locomotive is filled with steam from the steam network of the site and the locomotive is ready for use as long as sufficient pressure is present in the boiler.

District Heating Networks

District heating networks are seasonally operated, mainly in the winter months. Denmark already has intensive linking of the power grid with the district heating networks. Excess amounts of electricity, mainly from wind power, heat up hot-water tanks through electrical resistance heating, which then support the seasonal winter heat supply. This results in a low number of cycles of the storage, but entry of renewable energies into the heat supply. This link between electricity and heat supply is considered to be of essential importance for energy grids with a very high proportion of renewable energy [5].

Industrial Steam Networks at Integrated Sites

Industrial sites with a high demand for process heat often produce their own heat on site. The corresponding power plants, usually modern cogeneration plants, are heat operated. The energy management of integrated sites is a complex mesh of different processes that are coupled together. A steam network at different pressure levels, and thus temperature levels, usually offers sufficient flexibility in capacity and performance for site-specific heat management. Plants whose operation requires higher temperatures than are accessible via steam systems are using their respective fuels directly.

Isolated Industrial Sites

The situation in isolated sites is different, because they have a high specific heat requirement and only a few possibilities to dissipate the heat. Here, relatively large amounts of energy accumulate in the form of heat at temperature levels that are no longer suitable for direct use in the process. This is especially true for industrial processes that operate in batch mode. Industrial sector-specific solutions for thermal storage are, e.g., wind heaters in the steel industry, regenerators in the glass industry, etc., the aim of which is to use a portion of the waste heat for heating the process air and thus to retain it for use in the process. Nevertheless, often significant amounts of waste heat arise for which no further use in the process is possible. Possible lines of development could arise from synergies. For example, high-temperature batteries operate more efficiently in such locations, and high-temperature electrolysis could cover a considerable part of the energy requirement for hydrogen production by utilizing the waste heat from the process facilities.

4.4.2 Sensible Thermal Storage

Sensible thermal storage units store energy in the form of sensible heat. The storage capacity is given by the product of the temperature difference, the heat capacity (depending on temperature), and the amount of substance. Therefore, the power consumption and dissipation of sensible thermal storage changes its temperature and thus the temperature of the discharged heat flow during the input/output cycles. The possibilities are substantially limited by the thermal stability of the applied materials. Here, both the stability of the storage material itself and the heat-exchanger are important. In particular, care must be taken that, even after many temperature cycles, good thermal contact between the storage material and heat-exchanger is maintained. Concrete storage units can be used up to 400 °C without problems. The unfavorable heat-transfer properties of solid materials limit the system performance. The use of liquid storage media (e.g., molten salt) is one way to reduce this problem. Liquid eutectic $NaNO_3/KNO_3$ (60/40 %) molten salts are used in solar thermal power plants to bridge the day/night cycle. In the Spanish Andasol II power plant 28 500 t $NaNO_3/KNO_3$ salt melt is used between 292 °C and 386 °C to maintain the power plant capacity at the rated capacity of 50 MW for 7.5 h. Development potential exists in the direction of further salt melts that allow higher operating temperatures. An overview of the characteristics of sensible heat storage units is given in Tab. 10.

For a number of applications, especially in solar thermal power plants, an increase of the working temperature of the heat transfer and heat storage systems is of considerable importance. Liquid metals, e.g., sodium, are presently investigated besides thermal oils and salt melts. Such systems have previously been explored extensively in connection with cooling systems in nuclear power plants. Compared to other heat-transfer media, new questions with regard to heat transfer and material stability arise, but liquid metals have the potential to expand the temperature range of sensible thermal storage significantly, albeit with higher costs.

4.4.3 Latent Heat Storage

Unlike sensible heat storage, latent heat storage uses phase transitions of the storage material. That means they heat up during the loading of the storage, but not higher than the temperature of the phase transition (e.g., during melting), until the transition is complete. Conversely (e.g., during solidification), the heat is released at a constant temperature level again. Latent heat storage units can therefore fulfil the function of a thermal rectifier. Latent heat storage units are currently used more in the lower temperature range, such as the temperature control of buildings, whereby encapsulated hydrocarbons, integrated into the plastering, help to compensate the daily fluctuations in temperature. During the day, the paraffin wax is melted by the sun and thus reduces the temperature increase in the building; at night, the paraffin wax solidifies and prevents excessive cooling. The advantage of a constant temperature level is at the same time their biggest disadvantage. A broadening of the well-defined temperature of the phase transition can be achieved by mixing similar compounds. Currently, mainly solid/liquid phase transitions are exploited. Again, the introduction of heat into the solid is the limiting factor in the power input of the storage system. Also, solid/gas and liquid/gas phase transitions can be used. Thereby, the transition temperature can be varied by the pressure level of the gas.

For some material systems the storage material can be used especially well because strong supercooling of the melt is possible. This significantly widens the usable temperature range. A known example is sodium acetate trihydrate, which is used in the familiar pocket warmers. The melting point is 58.5 °C, but the melt can be cooled to –20 °C, and crystallization can be caused by seeding or mechanical action. Sodium acetate is

Table 10. Properties of storage materials for sensible heat; adapted from [111].

System	Melting point [°C]	Temperature range [°C]	Density ρ [g cm^{-3}]	Specific heat capacity [kJ kg^{-1}K^{-1}]
Water	0	0–100	0.98	4.19
Thermal oil	–70/–10	Up to 350 (boiling point)	0.87	2.1
53 KNO_3/40 $NaNO_2$/7 $NaNO_3$ [conc.]	142	Up to 450 (decomposition)	1.85	1.3
Na	98		0.84	1.26
Cast iron	1150–1300		7.2	0.54
Aluminum	660		2.7	0.92
Fireclay			2.1–2.6	1.0
Al_2O_3	1700		3.0	1.0
MgO	1700		3.0	1.0
Natural stones			1.9–2.6	0.8–0.9
Concrete				0.9

already used industrially in containers for the use of industrial low-temperature waste heat. The container with the molten salt is then transported to a location with heat demand (swimming pools, schools), where the heat of the salt is released again by solidification.

4.4.4 Adsorption Storage

Adsorption storage units use the heat generated by the absorption of a substance (e.g., water vapor) on a suitable support (e.g., zeolites or hydratable salts). The storage unit is loaded by desorption of the adsorbed molecules by heat supply and can be kept spatially separated from the adsorbent. For discharging, the two substances are brought together again. Adsorption takes place and the resulting heat can be used. Adsorption storage units also allow heat transformation, i.e., the heat emission (discharge) can be performed at a different temperature level than was used for loading. The temperature can be partially adjusted by means of the composition of the mixture of heat carrier medium (e.g., air) and adsorbate (water vapor). When using such storage systems mass and heat transfer are essential aspects of the system design. On a relatively small scale (construction of apartment buildings) zeolites are already being tested in thermal applications, but generally the adsorptive cooling of interior rooms is in the foreground of their applications.

4.4.5 Chemical Reactions for Heat Storage

Heat storage can also be implemented on the basis of chemical reactions by utilizing the reaction enthalpy of a reversible reaction system. Depending on the viewpoint, some of the above-mentioned adsorption systems can also be regarded as reactive storage systems. The advantages of storage systems based on chemical reactions are much higher accessible energy densities and higher temperature levels. As in the case of the adsorption accumulator, in the simplest case the heat supply during loading is often used to decompose the compound into two components that can be readily separated from each other (e.g., gas and solid). The components can be stored separately for a practically unlimited time. For discharge they are recombined and the heat of reaction dissipated. Here, too, the temperature level can be adjusted by varying the pressure levels of the gaseous reactants in the charge and discharge steps. The challenges in using chemical reactions as storage media are in the handling of the process and efficient energy uptake of the solid.

A number of such reversible heat storage systems were studied extensively in the context of high-temperature nuclear reactors many decades ago. An overview of the main systems developed up to 1990 was given by Bogdanovic et al. [112] (Tab. 11); more than 200 thermochemical cycles have been studied to greater or lesser extents [113]. Not all of these cycles are well-suited for longer-term storage of thermal energy.

The last entry in the table, the thermal dehydrogenation of metal hydrides, is discussed intensively in the cited literature. Such systems offer the possibility of storing heat energy with

Table 11. Heat-storage systems based on reversible chemical reactions; adapted from Bogdanovic et al. [112].

Reaction type	Examples	Temperature range [°C]	Specific energy density [kJ kg^{-1}]
Catalytic or thermal decomposition	$SO_3 \rightleftharpoons SO_2 + \frac{1}{2}\,O_2$	520–960	1235
	$NH_4HSO_4 \rightleftharpoons NH_3 + H_2O + SO_3$	927–427	2011
Steam reforming of methane (Eve-Adam)	$CH_4 + H_2O \rightleftharpoons CO + 3\,H_2$	480–1195	6053
Dehydrogenation of ethane or cyclohexane	$C_2H_6 \rightleftharpoons C_2H_4 + H_2$		
	$C_6H_{12} \rightleftharpoons C_6H_6 + 3\,H_2$		
Dehydration of metal hydroxides, salt hydrates, acids, and zeolites	$Ca(OH)_2 \rightleftharpoons CaO + H_2O$	572–402	1415
	$MgCl_2 \cdot 6\,H_2O \rightleftharpoons MgCl_2 \cdot 4\,H_2O + 2\,H_2O$		3180
	$H_2SO_4/H_2O \rightleftharpoons H_2SO_4 + H_2O$		
	Zeolite/$H_2O \rightleftharpoons$ Zeolite + H_2O	50–150	974–1370
NH_3 elimination from salt ammoniates	$CaCl_2 \cdot 8\,NH_3 \rightleftharpoons CaCl_2 \cdot 4\,NH_3 + 4\,NH_3$	32–100	745
Thermal decomposition of metal carbonates	$CaCO_3 \rightleftharpoons CaO + CO_2$		1780
	$MgCO_3 \rightleftharpoons MgO + CO_2$	427–327	1200
Thermal deoxygenation of metal oxides	$Na_2O_2 \rightleftharpoons Na_2O + \frac{1}{2}\,O_2$	650–975	1537
	$2\,KO_2 \rightleftharpoons K_2O + 1{,}5\,O_2$	300–800	2148
	$BaO_2 \rightleftharpoons BaO + \frac{1}{2}\,O_2$	300–825	528
Thermal dehydration of metal hydrides	e.g., $MgH_2 \rightleftharpoons Mg + H_2$	300–500	3200

high storage density at different temperature levels, whereby the temperature of the reversible phase transition can be adjusted by means of the hydrogen pressure. MgH_2 is the best-studied system, and has already been tested on a pilot scale for almost 2000 cycles, but also numerous other hydrides offer potential in this direction. MgH_2 can be used at temperatures between 300 and 500 °C, depending on the operating pressure, and the addition of other metals can shift the usable temperature in a wide range. The storage densities that can be achieved by using metal hydrides are comparatively high. Thus, the 28 500 t of molten salt in the Andasol II power plant could be replaced by about 1100 t of magnesium.

Hydride storage materials could be especially interesting in solar thermal power plants, in which hydrogen is generated in addition to the heat generated via thermochemical cycles, because in such cases, a hydrogen infrastructure is already in place. Such a solar thermal power plant could even produce on-demand electric power or hydrogen, or store some of the heat energy.

4.4.6 Advantages of Thermal Storage

Thermal storage systems can make an important contribution to increasing energy efficiency in the industrial, power generation, and building sectors by utilizing waste heat. They can use the transport and storage capacity of the district heating and steam networks and supply negative balancing energy for the power grid via resistance heating. This can make an important contribution to the integration of renewable energies into the heating sector. With the coupling of the electricity grid, heat storage, and district heating networks, Denmark has already extensive experience in the coupling of wind energy with the heating sector. Thermal storage is interesting as a single technology for certain applications, but can especially increase overall energy efficiency by linking system components.

4.4.7 Disadvantages of Thermal Storage

Most thermal storage systems for high temperature ranges are based on solid materials. The performance of the system, both for charge and discharge, is limited by heat transfer in the storage material (Tab. 12). The relatively low energy density of thermal storage results in large system volumes for high capacities. Another factor in the storage requirements is the temperature level of charging and discharging. In the industrial and power plant sectors thermal storage systems are case-by-case solutions, which makes further distribution difficult. Permanent storage of heat is only possible through the use of chemical reactions as storage systems. The transport networks for heat are connected only locally and operated by local operators, often on a seasonal basis.

Table 12. Properties of thermal energy storage systems.

Storage system	Storage principle	Temperature range	Advantages	Disadvantages	Applications
Hot-water tank	Heat capacity	> 100 °C (without pressure)	Attractively priced; stability due to vertical, density-dependent stratification; aquifer storage; link with existing infrastructure	Low storage density; *T* is a function of load	Heating of buildings
Steam accumulator	Vapor/liquid phase transition of water	Depending on the pressure level: low, medium, high	Attractively priced; link with existing infrastructure	Low storage density; T is a function of the pressure level	District heating and industrial heat supply
Sensible heat storage	Heat capacity	Limited by thermal stability of the material, e.g., concrete < 400 °C; $NaNO_3$/KNO_3 molten salt < 600 °C	Easy to use	*T* is a function of load	Industrial use (regenerators, ho-blast stoves, etc.); solar thermal power plants; adiabatic compressed-air energy storage
Latent heat storage	Phase transition	*T* defined by sharp transition	Constant temperature at charging and discharging; easy to use	Material properties (e.g., flammability)	Hand warmers, air conditioning
Adsorption storage	Adsorption heat	30–200 °C	Heat transformation	Handling of gas under pressure	Dishwashers, mobile heat storage
Chemical reactions	Reaction enthalpy	120–1400 °C	High energy density; heat transformation	Handling of gas under pressure	

4.5 Providing Flexibility through Energy-Intensive Processes as Storage Systems

4.5.1 Demand-Side Management/Demand-Side Response: Providing Balancing Power by Means of Electricity-Intensive Chemical Processes

Energy-intensive processes are already frequently run in a reciprocal rhythm to the average load curves. However, the power for these processes is usually secured by medium- and long-term supply contracts, which already take account of this procedure. Energy-intensive industries can additionally contribute to the stabilization of the power grid by further adjustment of production and thus their power requirements. This possibility is currently used only partially. The economic incentive for companies lies in the optimization of energy costs. Through demand-side management favorable electricity prices can be achieved. The associated grid stabilization is a side effect of the agreement, not the main objective. This is not about freely available balancing energy that network operators can access as needed since the decision is adapted to the needs of the industrial enterprise and not primarily aimed at grid stabilization.

In principle, energy-intensive processes can offer balancing energy, i.e., a demand-side response. Depending on the type of balancing energy, they must fulfill certain conditions and sign a contract with the transmission system operators in advance. The current list of companies offering balancing energy in agreement with the transmission system operators (primary (P), secondary (S), and tertiary (T) control power (CP)) is available in [16]. Besides operators of pumped hydroelectric power-storage plants or power plants as well as public utilities, only a few industrial companies are involved. As of 7.2.2017, these companies were from the metal sector (ArcelorMittal Eisenhüttenstadt GmbH (TCP), Nordenhammer Zinkhütte GmbH (SCP), ThyssenKrupp Steel Europe AG (TCP), Trimet Aluminium SE (PCP)) as well as the chemical industry parks CURRENTA GmbH & Co. OHG (TCP), Evonik Industries AG (TCP) and Infraserv GmbH & Co. Höchst KG (PS).

In addition, industrial plants can act as interruptible loads and thereby help to stabilize the grid. The possible contribution of different sectors depending on the turn-off period is estimated by the Research Institute for Energy to be 2.8 GW [114]. The available power is highly dependent on the turn-off period, as shown in Fig. 28. For the chemical industry, in this case, partial-load operation of chlor-alkali electrolysis and air separation were considered [115]. There have been discussions about the really accessible contribution by industrial plants [116]. A re-evaluation of the industrial potentials is subject to current research activities.

Energy-intensive processes can make a significant contribution to flexibility in the power grid. Unlike for conventional balancing energy, the following solutions still focus on the production of the desired products. However, the options presented permit the provision of flexibility for the power grid, both in terms of performance and capacity, due to lower marginal cost than possible when building a new isolated storage unit. The potential is not only limited to the chemical industry. Other energy-intensive industries could exploit similar opportunities. Adjustment may be gradual, considering the marginal cost, and thus corresponds to the fluctuations caused by the expansion of renewable energies.

4.5.2 Oversized Production Capacity in Processes with Continuous Operation

Whereas classical demand-side management or demand-side response is based on the restriction of energy-intensive processes, in this case the plant would deliberately be designed with a slight overcapacity. The aim would still be to produce the desired amount of product on average, while the actual production intensity is adjusted to a certain extent to the electricity supply. A relatively small additional investment (oversizing) compared to a power-to-gas system specifically installed for this purpose is counterbalanced by the benefits of a lower average cost for the electricity consumed and the flexibility for the power grid.

Large-scale, flexible, continuous processes, such as chlor-alkali electrolysis and air separation, in which the energy costs dominate compared to investment and other operating costs, are suitable. The German production capacity of chlorine by chlor-alkali electrolysis in membrane processes is 3352 kt a^{-1} [117]. At full capacity, this corresponds to a quantity of electricity of around 8 TWh (2.4 MWh t^{-1} chlorine), i.e., a power consumption of about 920 MW, or approximately 1.5 % of the current German net electricity consumption (530.9 TWh in 2015 [21]). A plant oversized by 10 % would have the same

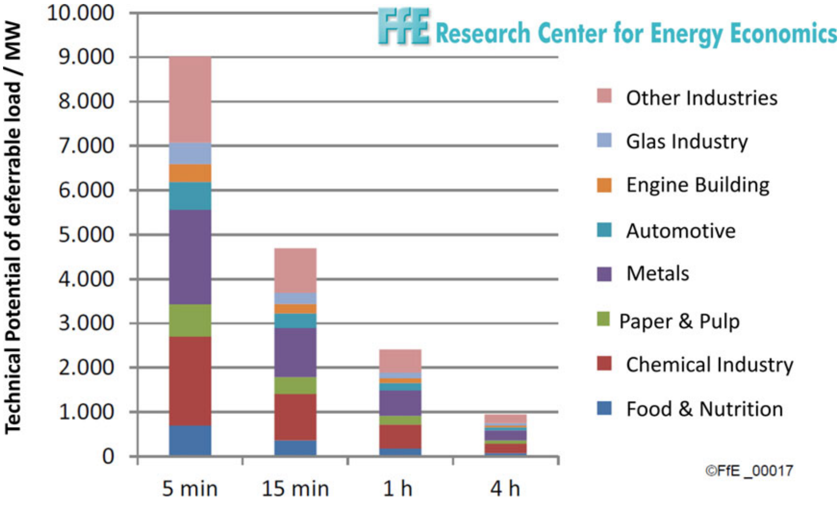


Figure 28. Technical potential of the turnoff power of industrial plants depending on the switch-off time [114]; © FfE e.V. 2011.

effect as an 85 MW pumped-storage power plant. Electricity costs contribute up to about 60 % of the total costs of chlorine production. The economics of oversized production plants are then better than those of existing installations if the savings in electricity costs due to appropriate remuneration for the supplied power is greater than the additional investment costs. This example clearly shows that the contributions of flexible process control at a certain oversizing are fix, especially in the energy sector.

Germany produces about 8000 kt of oxygen annually by air separation. At an electric power demand of 638 $\mathrm{kWh\,t^{-1}_{O2}}$, this corresponds to a quantity of electricity of 5 TWh and a power input of 600 MW, i.e., in the order of a fossil-fuel power plant.

4.5.3 Hybrid Processes

Hybrid processes are designed so that they can vary the source of the energy input. Thus, e.g., the required process heat can be supplied electrically or by burning natural gas, depending on prices. Usually, electricity is approximately 2.5 times more expensive than natural gas. In times of large power excess, this relationship may also be reversed. Decisive for the economy of a hybrid process is the decrease in average energy costs relative to the extra investment costs.

4.5.4 Temporal Shift of Energy-Intensive Batch Processes

Shifting the production of energy-intensive batch processes to times of favorable electricity prices is already carried out to some extent today, since it is in the interest of the operator to lower costs. The additional potential is difficult to estimate, since possible additional costs, such as night and weekend surcharges for the operating team, could greatly contribute to production costs in individual cases.

4.5.5 Economics of Fluctuating Industrial Processes

Adaptation of production to a fluctuating power supply can be of advantage for processes in which the energy costs represent a large fraction of the production costs, provided that the average energy costs of the product are significantly reduced. Therefore, the lower degree of utilization due to fluctuating operation must be compensated by correspondingly reduced energy costs. This is shown in simplified form in Fig. 29. The proportional costs, i.e., those that are linearly related to the amount of product produced, include, e.g., the electricity costs. In normal operation a maximum degree of utilization is aimed at keeping the fixed operating costs of the plant per unit product as low as possible. The profit margin as the difference between the costs and the recoverable price is maximized. A discontinuous mode of operation leads to a reduction of capacity, as indicated by the horizontal arrow (from 100 to approximately 65 %) in Fig. 29. In the example shown, the discontinuous mode of operation will be rewarded by a reduction of 25 % of the average electricity costs. Thus, up to a certain reduced degree of utilization, an equal or greater profit margin per unit product can also be achieved. However, if free capacity decreases below this value, then discontinuous operation is no longer worthwhile compared to normal operation.

The profit margin per unit of product still must be multiplied by the total production of the period considered. Here, a reduced overall profit can lead to a lower degree of utilization despite a higher profit margin per unit of product, since less product was made and sold in the period. This is shown schematically for the above example in Fig. 30. The horizontal arrow only allows a smaller reduction in capacity (approximately 80 %) if the total profit is kept constant. In the present discussion, it was neglected that the frequent startup and shutdown procedures of a fluctuating operating mode generally reduce the efficiency of the process compared to the optimum steady-state operating point.

This schematic argument based on the costs neglects the predominance of energy-intensive processes in the basic industries, such as the steel industry and the chemical industry. The relevant products are often at the very beginning of the value chain and are transformed into a variety of final products in subsequent steps. Often the raw materials are processed further in situ. Discontinuous raw material production would either be reflected in the downstream processes, which would also have to be carried out batchwise, but could not take advantage of the cost benefits of reduced energy costs to the same extent. Or adequate storage capacities would have to be present to ensure uninterrupted production of the downstream processes. Therefore, any adaptation to a fluctuating power supply should be implemented as early as possible in the value chain, either by

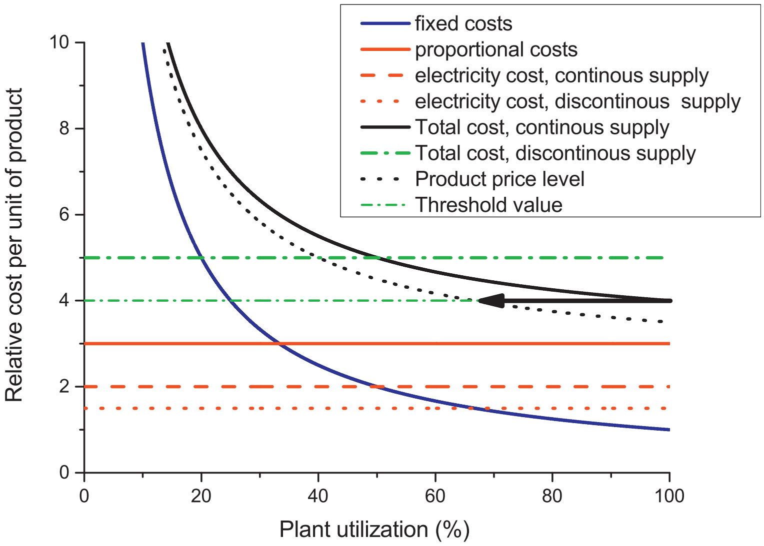


Figure 29. Schematic representation of the effect of fluctuating operation on the cost structure per product unit.

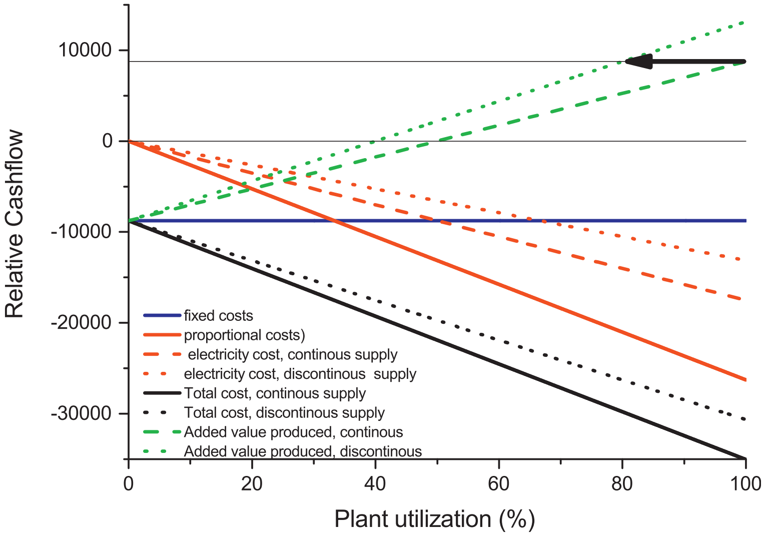


Figure 30. Schematic representation of the effect of a fluctuating operation of a production plant on the cash flow.

buffering the power supply directly or through appropriate storage at the earliest possible point in the value chain.

This may in particular be useful if a market-related underutilization of the plant (or an intentional overcapacity) allows the opening of cost reduction potentials through fluctuating operation. This holds true, of course, only as long as the supply of customers with the product can be assured by adequate storage.

These considerations are not limited exclusively to the power supply. An example from the chemical industry of the adaptation/buffering of the production to fluctuating energy prices is the plant complex of DOW Olefinverbund in Teutschenthal, where ethylene and propylene are discontinuously produced from crackers, depending on the raw material price, and are then temporarily stored in caverns for continuous downstream processes.

Economically, the advantage of grid stabilization is associated with a loss of value through lack of production along the value chain. Therefore, compared to a production adjustment, other alternatives, such as the down-regulation of electricity, supply of reserve capacity, etc., should always be evaluated as well.

4.6 Storage as a Grid Service Provider and Grid Transfer Technologies

4.6.1 State of the Art

Currently, the various energy grids (e.g., gas and power grids) are essentially operated independently. They are considered to be both technically and economically independent of each other. From this perspective, the grids are usually used unidirectionally (from supplier to consumer) in a certain supply structure. Bidirectional operation is currently partially used in the power grid, for which the local supply from renewable energies can lead to a net reversal.

4.6.2 Links between the Grids

The energy storage technologies presented above open up the possibility of linking the separate energy grids into a common system. Apart from the function to save an amount of energy in a timely manner, many storage technologies can also act as energy transfer technologies. Thereby, the specific advantages of the different grids for stabilization can be used by the whole system. For example, power-to-gas processes decrease the amount of electricity not currently usable by any consumer (surplus power) and allow storage of the energy in the gas grid, which has significantly more capacity than the electricity grid. Conversely, gas turbines can generate electricity when needed.

A common systematic evaluation of grids and storage technologies allows greater flexibility in all grids and more efficient use of energy since the specific advantages of each form of energy can be better exploited. For this purpose, energy transport in the grids must be generally bidirectional. Thereby, new options arise through storage technologies, e.g., thermal or electrical operation of cogeneration plants without discarding/compensating the surplus/deficit of the other form of energy. This link leads to improved security of supply, as a specific undersupply or oversupply can be better balanced within certain limits. With regard to climate change, a well-linked integrated system should lead to lower specific emissions per unit of energy than the isolated individual systems.

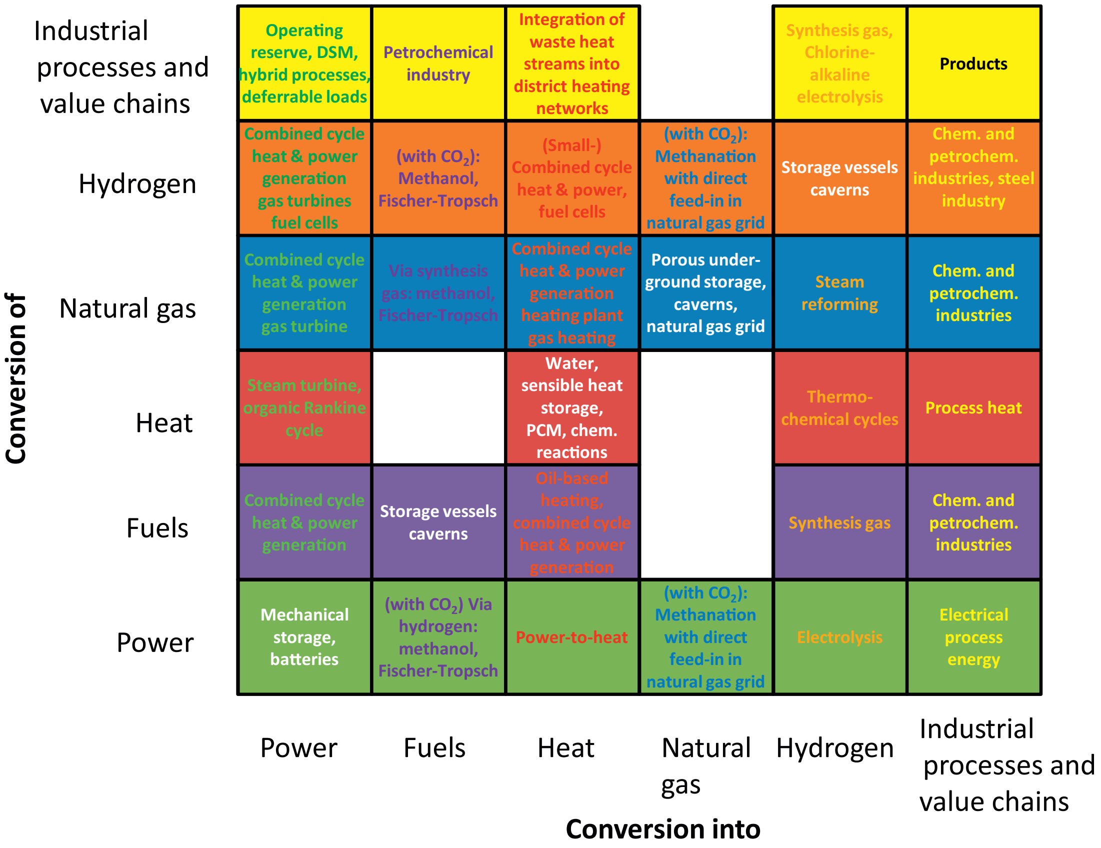
However, each conversion is associated with energy losses and additional costs and must therefore also be critically evaluated from an economic perspective. Whether a transformation that is technically possible is also economically viable must be examined in each individual case.

Furthermore, it should be noted that in a coupled system other cost and revenue structures occur than in the isolated individual systems. Existing business models will have to adapt to the integrated structure.

Not all grids benefit from a system evaluation to the same extent. Grids with few means of compensation will benefit more than those that can already flexibly adapt to major fluctuations. The power grid will benefit most from the links since options for storing electricity are still very limited. In contrast, the benefits will be less important from the perspective of the stability of the gas grid. The various grid cross-links and related technologies are schematically shown in Fig. 31.

4.6.3 Economic Conditions for the Use of Storage Technologies in the Power Grid

Currently, the storage facilities in the power grid are almost exclusively pumped-hydro storage power stations. This will continue in the foreseeable future to be the most cost-effective storage technology in the power grid. In particular owing to the massive expansion of photovoltaics, which has its peak production around midday, the business model of the operators of pumped-storage power stations (storing cheap electricity at



Conversion of / Conversion into	Power	Fuels	Heat	Natural gas	Hydrogen	Industrial processes and value chains
Industrial processes and value chains	Operating reserve, DSM, hybrid processes, deferrable loads	Petrochemical industry	Integration of waste heat streams into district heating networks		Synthesis gas, Chlorine-alkaline electrolysis	Products
Hydrogen	Combined cycle heat & power generation gas turbines fuel cells	(with CO_2): Methanol, Fischer-Tropsch	(Small-) Combined cycle heat & power, fuel cells	(with CO_2): Methanation with direct feed-in in natural gas grid	Storage vessels caverns	Chem. and petrochem. industries, steel industry
Natural gas	Combined cycle heat & power generation gas turbine	Via synthesis gas: methanol, Fischer-Tropsch	Combined cycle heat & power generation heating plant gas heating	Porous underground storage, caverns, natural gas grid	Steam reforming	Chem. and petrochem. industries
Heat	Steam turbine, organic Rankine cycle		Water, sensible heat storage, PCM, chem. reactions		Thermochemical cycles	Process heat
Fuels	Combined cycle heat & power generation	Storage vessels caverns	Oil-based heating, combined cycle heat & power generation		Synthesis gas	Chem. and petrochem. industries
Power	Mechanical storage, batteries	(with CO_2) Via hydrogen: methanol, Fischer-Tropsch	Power-to-heat	(with CO_2): Methanation with direct feed-in in natural gas grid	Electrolysis	Electrical process energy

Figure 31. Areas of energy applications in the form of a matrix. In the fields, the respective storage or conversion technology is indicated by which the energy or storage forms can be transformed into each other or integrated into industrial processes. For example, electricity (row) is made available through power-to-heat in the form of heat (column).

night and releasing it when demand is high, i.e., around noon) has come under massive pressure.

Simultaneously, the feed priority for electricity generated from renewable energies leads to a general lowering of the market price of electricity because it covers a part of the demand, but the EEG electricity volume has no associated price. The current price building on the electricity exchange thus takes place for a reduced demand instead, at a (surplus) supply by conventional power plants. Thereby, those power stations come into play that have the lowest marginal cost for the required amount of electricity, that is, usually written-off nuclear power stations and coal-fired power stations. The normal electricity consumers do not benefit from the reduced price of electricity, as they must pay the EEG levy for the remuneration of renewable power generation, which is significantly higher than the current market price of electricity.

Generally speaking, for a storage technology the development of the maximum and minimum electricity prices on the stock exchange is reflected in the marginal costs and the potential profit margin. Since currently even pumped-hydro storage power plants find it difficult to operate profitably, this is a challenge that should not be underestimated for any storage technology. Under the current conditions, the introduction of new storage technologies into the power grid is not economical [33].

The grid-stabilizing effect of storage systems is currently not included in the pricing of electricity. This corresponds to system service in terms of increased security of supply, the positive effect of which is hard to express financially. For a review of the system services and the development of appropriate business models, it is necessary to reach a broad social consensus on the definition and the desired level of security of supply.

4.6.4 Energy Storage in Steam and District Heating Grids

Industrial steam and hot-water grids are created as transport and distribution networks and have only a small inherent storage capacity. The heat is provided on demand and transported to the appropriate users via the grids. The storage capacity is determined by the amount of heat-transfer material, i.e., water or steam, and the temperature level. In general, industrial steam systems have a buffer capacity of a few minutes of the given heat demand. By means of power-to-heat systems, however, electrical energy can be converted to heat and supplied to consumers via the grid. For the most efficient use of the electric energy, conversion to heat at the highest possible temperature level is desirable. The heat supplied by power-to-heat systems substitutes heat provided by conventional means, which in turn reduces the amount of fuel consumption and related CO_2 emissions. Therefore, a power-to-heat system in this context can also be regarded as an inverse power-to-gas system, in terms of natural gas saved. In combined-cycle power plants this process can allow staggered exclusive operation of the steam turbine by using a thermal storage system. Depending on the required operation of the power plant, this can be a beneficial option.

5 Reference Cases for the Use of Energy Storage

Below, different reference cases are considered and the possible use of energy storage systems is exemplified and evaluated. However, these reference cases cannot serve as a substitute for a detailed individual analysis.

5.1 Electricity Supply of a Household through Photovoltaics

The average household in Germany in 2015 consumed around 24 050 kWh of energy at a total cost of almost 2744 € a^{-1} [21]. The largest energy share is accounted for by space heating, which is seasonally dependent and required mainly in the winter, and fuels for mobility (Fig. 32 a). In contrast, electric power with 3235 kWh [21] (approximately 10 kWh d^{-1}) accounts for only a smaller percentage, which, however, makes up a disproportionate share of the cost (Fig. 32 b) with about one-third of the total energy cost of the average household. In 2015, the average electricity price for households was 28.70 ct kWh^{-1} [118], and thus the average electricity bill of a private household was € 928. A reduction in the cost of electricity can therefore be a promising approach to reducing the overall energy costs of the household.

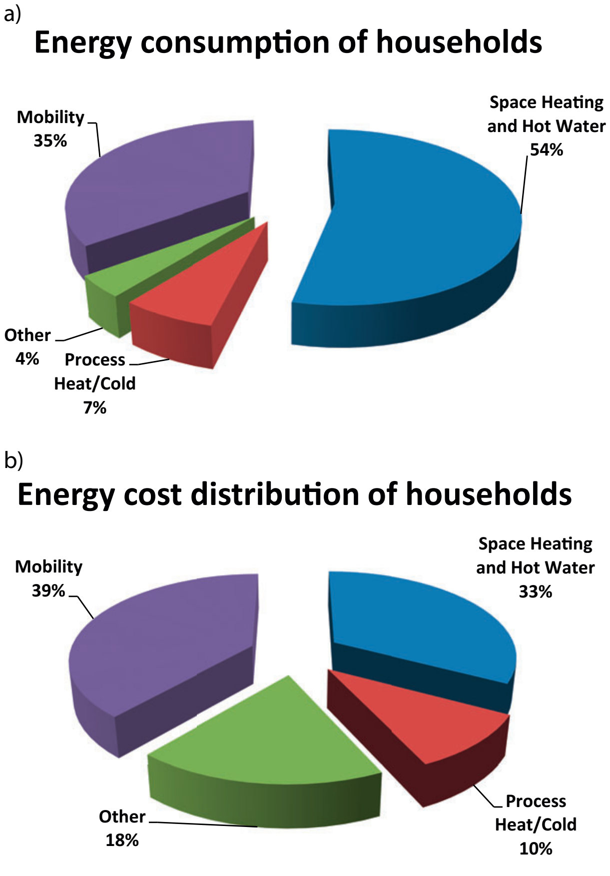


Figure 32. (a) Use of energy and (b) distribution of energy costs for an average household (2015).

5.1.1 Operation of a Photovoltaic System

One possibility could be the creation of the required electricity by an appropriately dimensioned photovoltaic system. Photovoltaics have low utilization in terms of full-load hours. In Germany, the utilization is around 808 full-load hours per year, so that a plant with a capacity of 4 kW should be enough to provide the required electricity for the year.

The power generation of the photovoltaic system occurs discontinuously and is not tailored to consumption. The photovoltaic power at any time depends on the sun and the solar radiation intensity. It varies greatly depending on the time of day and season. In contrast, the consumption of an average household (Fig. 33.), although variable as a function of the time of day, is relatively constant over the seasons.

According to the EEG, photovoltaic power has feed-in priority, so that all the electricity generated can be supplied to the power grid at any time for the legally guaranteed price. At the current state of the EEG compensation or price of electricity (max. 12,56 ct kWh^{-1} (January 2015 [119], new plant) or 28.70 ct kWh^{-1} (electricity price 2015), respectively), the net annual electricity costs of the household of € 928 would be reduced to € 522 (difference between current price and remuneration: 16.14 ct kWh^{-1} multiplied by 3235 kWh annual electricity demand/generation).

If the electricity generated is primarily used for self-sufficiency, the surplus electricity is only fed into the grid in times of excess, and in times of insufficient generation the corresponding amount of electricity is obtained from the grid. In this case, the cost of electricity for the household drops to € 304.

The consideration of the profitability of an investment in the photovoltaic system from the perspective of the household is not the focus of attention here and is only briefly touched on. € 1600 per kW_p (kilowatt peak power) + 19 % VAT is assumed for the investment cost of the plant [120]. This results in investment costs of € 8000. This is offset by annual savings of € 449 for a period of 20 years based on the EEG compensation in the event of complete supply to the power grid. Without considering other operating costs, this corresponds to a return on investment of 0.58 %. In a system primarily used for self-sufficiency, the yield is even as high as 5.44 %.

5.1.2 Use of Storage Systems in the Household

As a household has to pay more for the purchase from the power grid than it receives in payment for supplying the grid,

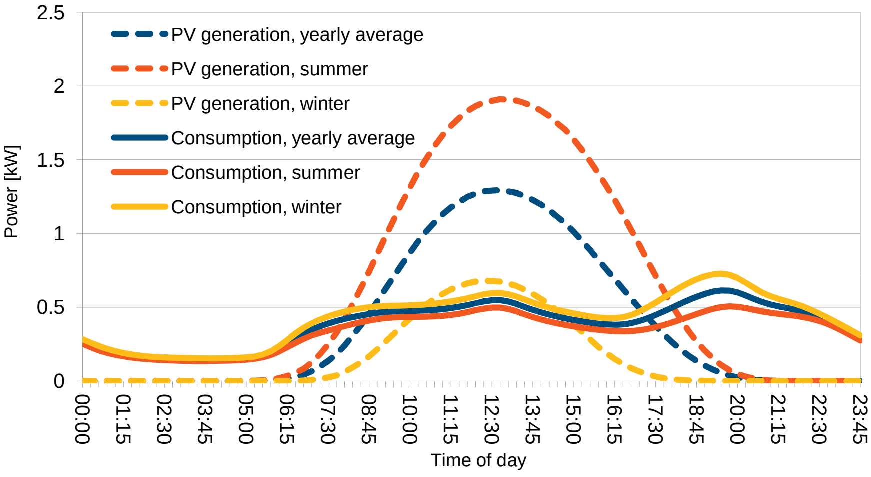


Figure 33. Exemplary photovoltaic generation and power consumption of a household in the winter and summer months, based on the data of 2011 [120]. The slight shift of the curve maximum of the photovoltaic generation is caused by the change from winter to summer time.

energy costs can be further reduced by storing the excess electricity produced for use during periods of insufficient production. The use of energy storage systems could meet this requirement with the aim of reducing the overall cost to the household further.

An overview of the seasonal variation of photovoltaic generation (Fig. 33) illustrates the problem. The average electricity production and the average power consumption of a household are balanced throughout the day. Thereby a storage requirement of approximately 60 % of the daily amount of electricity (about 6 kWh) to fully cover the consumption at night could be deduced. However, this approach does not adequately consider the seasonal variation of the photovoltaic power. On an average summer day, many times more electricity is generated than on an average winter day. A series of summer days would tend to overcharge the storage unit, while a series of winter days would result in a constant discharge of the storage system.The challenge of storage usage thus lies not only in the operation of storage units with relatively low capacity, but also in the function of seasonal storage systems to provide enough power on sunless winter days.

5.1.3 Electrochemical Storage Systems

As storage technology for households primarily electrochemical storage is considered. Firstly, both the produced and used energy form is electricity; therefore, additional conversions are avoided. On the other hand, electrochemical storage units are fast enough to react to variations in power generation (e.g., due to passing clouds). The performance requirements for a household lie in a range that can be well covered by electrochemical storage systems. On the other hand, the costs of electrochemical storage devices are mainly determined by the required amount of storage material, i.e., the storage capacity.

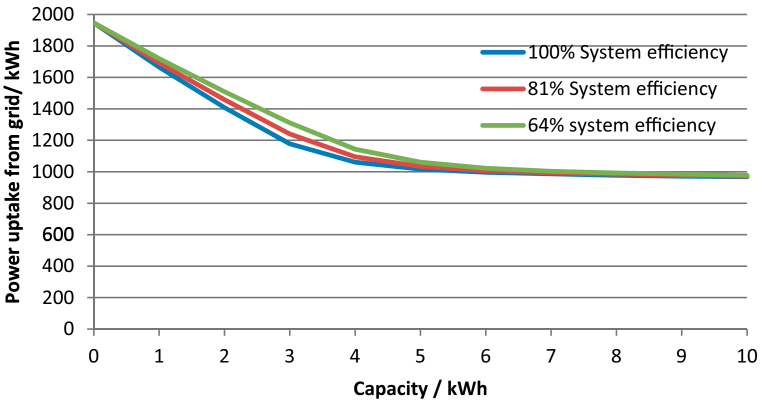


Figure 34. Effect of the storage on the purchase of electricity from the grid.

On the basis of the photovoltaic generation data of 2011 [121], the effect of battery systems of different capacities can be demonstrated. Using a relatively small storage unit allows the electricity supplied by the power grid to be reduced by about half. A larger capacity leads only to a slight further decrease of electricity purchases from the grid. At small capacities, a storage unit is often fully charged and discharged, but at higher capacities the number of full-load cycles is reduced. The efficiency of storage technology plays only a subordinate role, as can clearly be seen in Fig. 34. A lower system efficiency corresponds to the energy balance of a storage unit with slightly smaller capacity. A design that would make the household self-sufficient in power would need a capacity on the order of 800 kWh, around a quarter of the annual electricity consumption.

Therefore, the construction of storage units on the basis of the capacity that would ensure an independent supply would be just as inappropriate as a design based on the performance at the maximum occurring peak power, in this example, approximately 2 kW. The maximum performance occurs on summer days, when the storage unit can no longer absorb these power peaks due to its low capacity.

For the following analysis, two different electrochemical storages were considered: lead-acid batteries and Li-ion batteries (Tab. 13). Lead-acid batteries have been widely used in the past for stationary power storage, in addition to their main application in the mobile sector. The costs benefit from the economy of scale and the many years of experience. The lifetime of lead-acid batteries is relatively short (3–5 years) and the cycling efficiency of the electrochemical storage process rather modest. Li-ion batteries are characterized by very high cycle efficiency, but also by higher investment costs. It was assumed that the investment costs in the considered power window scale up linearly with the capacity of the battery system.

Table 13. Properties of lead-acid batteries and Li-ion batteries.

Parameter	Pb-acid	Li-ion
Power consumption, power output [kW]	1	1
Electrical cycle efficiency [%]	87	96
Calendrical life [a]	4	20
System price of storage capacity [€ kWh^{-1}]	75	600
Annual return on the capital invested [%]	6	6
Other operating expenses as a percentage of investment costs [%]	2	2

From Fig. 35 it becomes clear that lead-acid batteries can reduce the overall costs. Li-ion batteries have decreased significantly in price, but still have higher investment costs so that they more than offset most of the savings generated in electricity costs. In the case of lead-acid batteries, the savings for the household are in the range of 59 € a^{-1} for a capacity of 4 kWh. Li-ion batteries achieve savings up to 20 € a^{-1} for a capacity of 3 kWh. If the investment costs of Li-ion batteries continue to fall, they will achieve similar savings as lead-acid batteries. Complete self-sufficiency of the household can be only ensured starting from a capacity of 730–870 kWh per year, depending on the cycling efficiency of the considered type of battery, which would cover the electricity consumption of around three months.

Although complete self-sufficiency through electrochemical storage is theoretically possible for the considered household, it is not economical. In contrast, a relatively small lead-acid battery could reduce the overall costs to the household. Li-ion batteries currently have too high costs per installed unit capacity to achieve the same-sized effect.

The effect of the small storage battery is best understood by examining the power-duration curve (Fig. 36) of the household. The residual load without the use of a storage unit is shown as a black line. In most hours of the year (in winter and at nights) the demand dominates (positive residual load, current is drawn from the grid), while in the daytime in the summer the photovoltaically generated electricity dominates (negative residual load, current is delivered to the grid). The other lines describe the effect of the storage for the different conditions. The different system efficiency has virtually no effect given the small capacity. Different power specifications result in only minor changes in the case of surplus production (negative residual load). The effect of the battery is shown most clearly in the central region of the curve. This behavior is typical of a storage system that is designed to compensate for short-term fluctuations. The division of the timeline describes 720 h each (30 d). Without storage, hours equaling nearly 8.5 months correspond to a load surplus, while for the equivalent of just over 3.5 months a production surplus is noted. The use of storage units reduces this time to 5 and 1.5 months. For the duration of 5.5 months demand and generation are balanced. The effect of storage is most pronounced in the middle area of the power-duration curve. This means that battery storage does not smooth out the extreme values, but the more frequently the minor fluctuations.

5.1.4 Power to Heat

An average household uses the largest amounts of energy for heating and to produce hot water (process heat, e.g., for cooking, is assigned to electricity consumption for the sake of

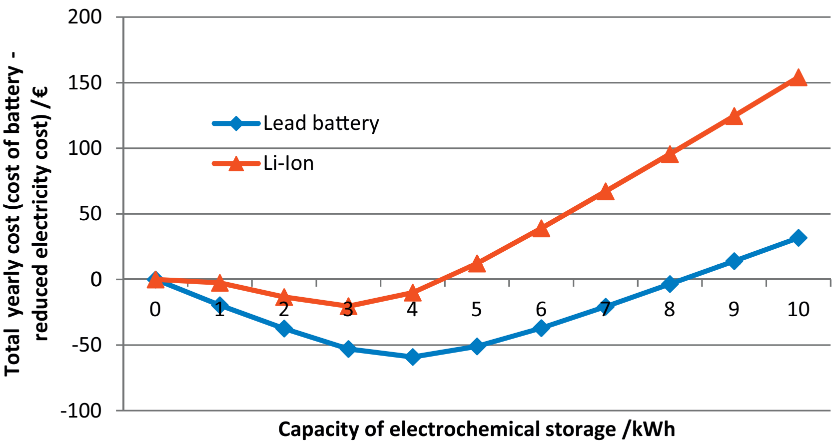


Figure 35. Comparison of the total costs of lead-acid batteries and Li-ion batteries for the storage of photovoltaic electricity in private households.

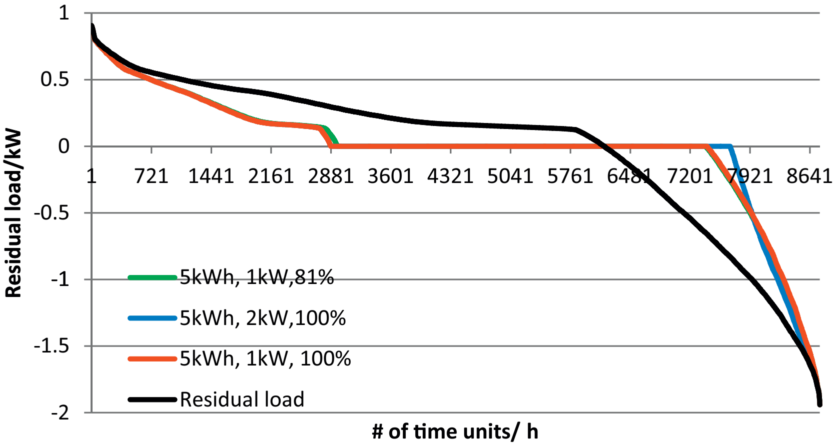


Figure 36. Power-duration curve for the use of an energy storage device in a private household.

simplicity). In total, this amounts to 12 931 kWh of heat. However, this accounts for only about 49 % of the energy costs of the household, so that average costs of 6.96 ct kWh^{-1} for heat can be assumed.

An argument against conversion of the surplus electricity generated by a photovoltaic system to heat, especially in the summer months, is the fact that the heat generated cannot be used, because the majority of the heat demand arises seasonally during the winter months. The daily requirement of hot water, which, for the sake of simplicity, is assumed to be constant, is 6.15 kWh. Unlike electricity, however, heat can be stored seasonally in the form of hot-water tanks.

Conversion of the generated electricity to heat can be done by simple heating coils with a conversion efficiency of close to 100 %, i.e., 1 kWh of electric energy is converted to 1 kWh of thermal energy.

An alternative possibility is conversion via a heat pump (Fig. 37). The heat pump evaporates a low-boiling working medium by using heat from the environment. The gaseous working medium is compressed (for this step power is needed) and heats up. The compressed working fluid condenses in the condenser and releases heat, e.g., as space heating or to hot-water tanks. Subsequently, the working fluid is expanded and the cycle begins again. The ratio of the amount of heat produced per unit of electrical power is described by the coefficient of performance. Typically, heat pumps for use in building heating reach a performance factor of four. The associated, apparently "nonphysical" efficiency is explained by the fact that the majority of the energy required comes from the environment (evaporation of the working medium).

Heat pumps are subsidized by power companies in the form of lower electricity prices, which lie approximately 5 ct under the regular budget price. With a performance factor of four, this results in an approximate price of 6 ct kWh$^{-1}_{\text{heat}}$ which is about 1 ct below the average costs of the households for heat. Conversely, this means that conversion of electricity to heat and subsequent storage promises a greater cost reduction than the supply of excess power to the grid at the given monetary compensation.

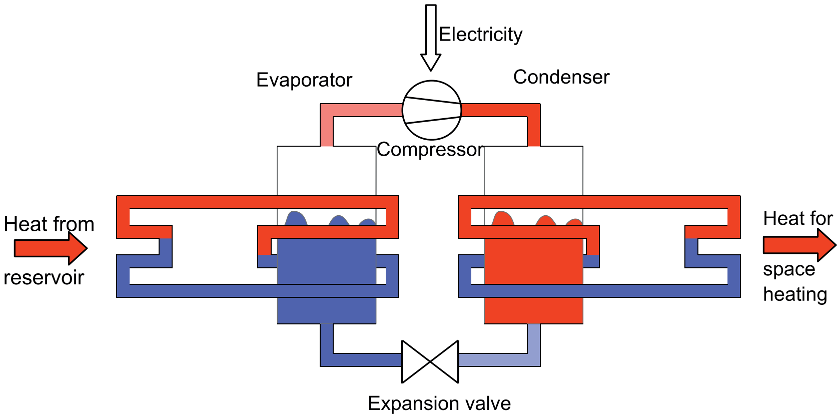


Figure 37. Schematic representation of the functional principle of a heat pump for heat recovery in the building sector [122].

5.1.5 Power to Gas

The efficiency of conversion of electricity to methane, provided a suitable CO_2 source is available, is max. 56 %, i.e., 1 kWh of electricity is converted to methane with a calorific value of about 2 MJ, corresponding to around 0.053 m^3 methane. At a household gas price of approximately 6.79 ct kWh^{-1} [21], this corresponds to a value of about 4 ct for the generated methane. The technologies for implementation on this scale do not presently exist. It is very unlikely that these technologies will advance to a cost range in which they are to operate economically for the case considered here.

5.1.6 Cost Considerations

For the chosen example, the marginal cost of energy storage technologies can be estimated relatively well. The EEG compensation provides a clear reference. The savings in personal consumption compared to complete supply to the grid are given by the difference between EEG remuneration and the current price multiplied by the self-used amount of electricity. The impact of the energy accumulator is an increase in self-used amount of energy, and thus the corresponding cost savings. Once the full costs of the storage are higher, a positive profitability is no longer ensured.

Fig. 38 shows the development of the energy costs for an average household depending on the configuration of the technologies. The first group describes the energy cost structure of an average household. The second group considers a photovoltaic system that produces the same amount of electricity as is consumed by the household during the year. The photovoltaic power is completely fed into the grid and covers the electricity consumption from the grid. The third group assumes self-consumption of produced electricity, feeding of the excess electricity into the grid, and supply from the grid to meet additional needs. The fourth group involves an electrochemical storage unit having a capacity of 4 kWh. The fifth group uses excess electricity to heat a water tank, while the last group converts excess current to methane, which is fed into the gas grid. The respective investment costs have not been included in the consideration. From this example, the marginal costs of capital and operating costs of the additional components are determined. Thus, the additional construction of a photovoltaic system leads to a reduction in energy costs of the household by around € 406. The self-consumption of the generated electricity reduces the costs by a further € 208, so that the construction of a photovoltaic system is worthwhile, as long as the annual operating and apportioned investment costs of the plant are below € 614. The installation of a battery storage unit (power: 1 kW, capacity: 4 kWh) is only worthwhile if its annual expenses are less than € 141 – a condition which is currently met only by lead-acid batteries. The use of excess electricity to charge a

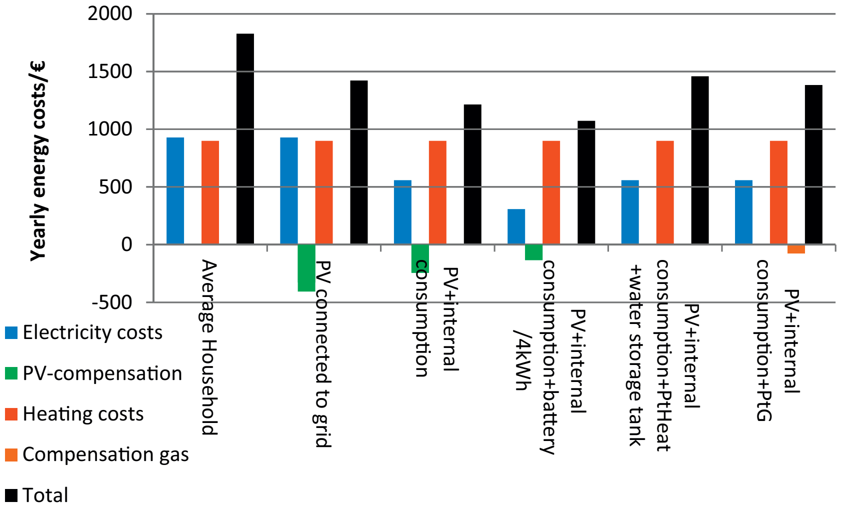


Figure 38. Annual energy costs of an average household (without the investment costs associated with the respective technologies).

heat accumulator (power to heat), e.g., via a heating coil, is not worthwhile, because the reduced heating costs (6.96 ct kWh^{-1}$_{\text{heat}}$) are significantly lower than the remuneration of photovoltaic power (12.56 ct kWh^{-1}$_{\text{electricity}}$). The same holds true for the conversion of electricity to methane (power to gas, CO_2 source required) including injection into the gas grid. Moreover, the low conversion efficiency of max. 56 % is a problem. In both cases, the energy costs are already higher than in the case of self-consumption of the generated photovoltaic electricity. The possible additional investment and operating costs for the necessary infrastructure are not considered in this analysis.

This description changes slightly when a heat pump is used to provide the necessary space heating and hot-water supply. The annual energy costs are generally slightly lower since the heat from the heat pump is slightly cheaper than alternative heat supply, e.g., a gas condensing boiler. The efficiency with which a heat pump provides heat from power makes the power-to-heat combination of a photovoltaic system with self-consumption (with/without battery) and a heat pump with a heat storage unit (hot-water tank) a conceivable option (Fig. 39). However, a careful examination must take into account the higher investment costs of a heat pump. The annual capital and operating costs of the seasonal heat storage should not exceed € 217. The use of an electrochemical storage may still contribute to a further reduction in energy costs, but the potential cost savings and thus the maximum investment and operating costs of the storage are still much lower at € 37 for simultaneous use of a heat storage.

5.2 Industrial Site

Besides households, the industrial infrastructure is a major energy consumer. In particular, energy-intensive industry for the production of basic materials (e.g., chemical industry, steel and metal production and processing, ceramics, glass, and building materials such as cement) require a secure and high-quality energy supply.

5.2.1 Description of the Industrial Site

The assumptions used in the following were derived on the basis of a real industrial site. It is located close to a major German city and has good access to the transport infrastructure via road, rail, and inland waterways. The industrial site covers about 460 hectares and provides employment for 22 000 people. A total of about 90 companies are represented in the industrial site, which have developed around a chemical-pharmaceutical core complex. Besides the actual production units, also commercial space, office buildings, training facilities, and research and development facilities including laboratories are energy consumers in the industrial site. The operator of the industrial site not only supplies the companies with energy, but also offers a range of other services such as the supply of media (water, technical gases, etc.), the internal transport infrastructure, a fire brigade, security services, and waste and wastewater treatment.

Clients are connected to a complex energy infrastructure that can serve a variety of applications. These include power grids at different voltage levels, gas, cold-water and hot-water supply, and a steam network at different pressure levels, with temperatures ranging up to 300 °C.

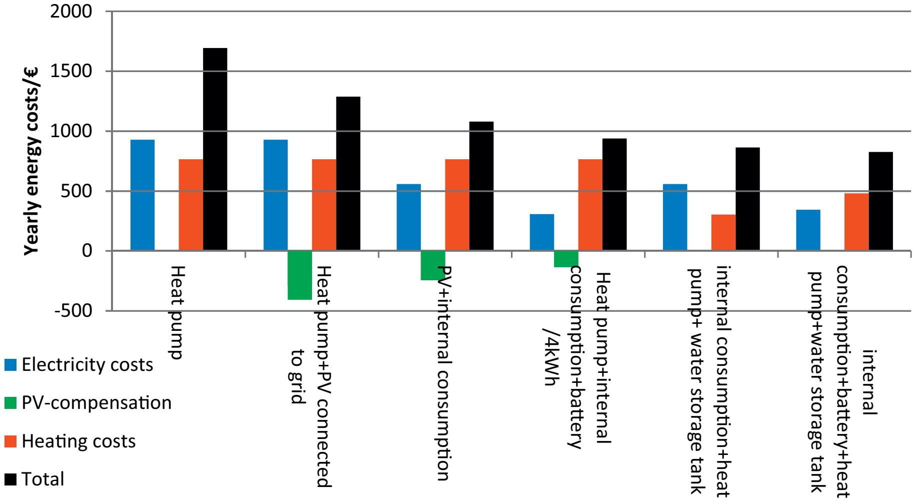


Figure 39. Energy costs of an average household using a heat pump to provide the heat and hot-water demand. The respective investment costs have not been included in the analysis.

The industrial park has an annual demand of 2000 GWh of electricity and 3200 GWh of heat. This roughly corresponds to the annual electricity needs of 670 000 households and a heat requirement of around 260 000 single-family homes.

The energy supply is generated by an integrated approach for electricity and steam, in which the capacity to generate electricity and steam as well as the consumers and suppliers are linked (Fig. 40). This concept also allows for the provision of balancing energy for the electricity market, as it can be compensated within the network without affecting the supply to consumers in the industrial park.

5.2.2 Possibilities for the Use of Energy Storage Technologies in Industrial Sites

In all industrial sites, the reliable supply of consumers and facilities with the required energy services is paramount. The possibilities for the use of energy storage in both the heat supply and power supply of an industrial park are very limited. The strong integration of the various processes of the existing energy networks and the desired continuous operation of the plants considerably reduce the fluctuations that would make the use of energy storage technologies feasible.

Thus, it can be assumed that the heat load profile contains only a small seasonal component, which arises mainly due to the additional demand for space heating during the cold season, since the demand for process heat is practically constant throughout the year. Due to the importance of the process heat for the installed production units, CHP plants in industrial parks are frequently operated in a heat-controlled mode, which offers only very restricted adaptability to fluctuations in the electricity grid. Due to their constant demand for heat, industrial sites are the ideal sites for CHP plants, which can use the energy content of the fuels with maximum efficiency.

The consumption and supply of electrical energy compared to other users in industrial parks varies only slightly. Large continuous consumers, such as chlor-alkali electrolysis, provide a constant load. A small daily variation may result from the operation of smaller batch plants. For the following discussion, it has been hypothesized that the daily fluctuations do not exceed 5 % of the average value. In the following discussion of an industrial site with an annual electricity demand of 2000 GWh, this variation is considered to be sinusoidal for the sake of simplicity (Fig. 41).

A storage unit or a combination of storage units for electrical energy to compensate for this load profile would pass through a cycle every day. The storage would require a capacity of 88 MWh, approximately 1.6 % of the daily amount of electricity, at a maximum power for charge and discharge of 11.5 MW.

For the heat supply a seasonal storage would be appropriate, which would have to store and discharge the heat at the temperature level of the steam network, i.e., at 300 °C, in order to optimally integrate into the infrastructure. A lower temperature level would be possible if its use would only serve to meet the demand for space heating. The storage system would pass through one cycle annually. If the heat demand of an industrial site is assumed to be sinusoidal over the year, similar to the above mentioned daily variation, then Fig. 42 results.

To compensate for such a seasonal thermal load profile, a thermal storage system would have to have a storage capacity of 51 GWh at a maximum storage and discharge performance of 18.3 MW. A total of about 1.6 % of the annual heat requirement would be stored in the storage units in the warm months and released for use in the cold months.

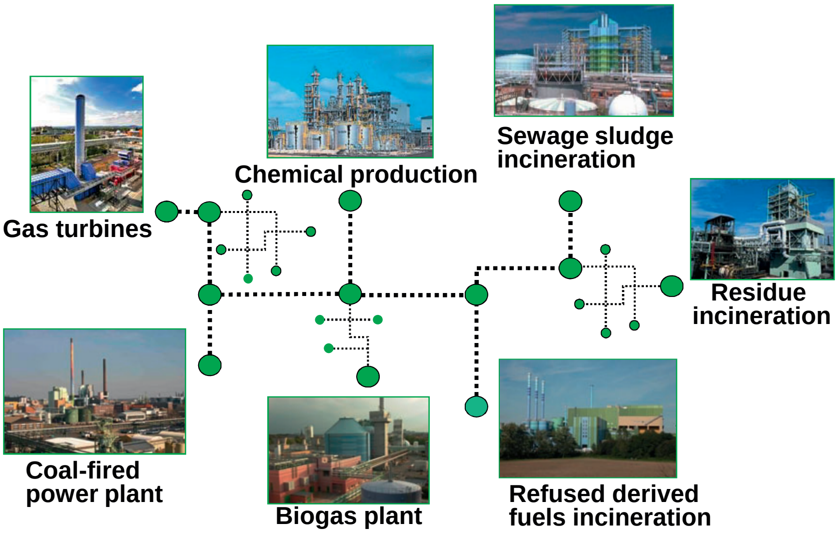


Figure 40. Schematic representation of the connections in the industrial park [123]; © Infraserv-Hoechst, 2014.

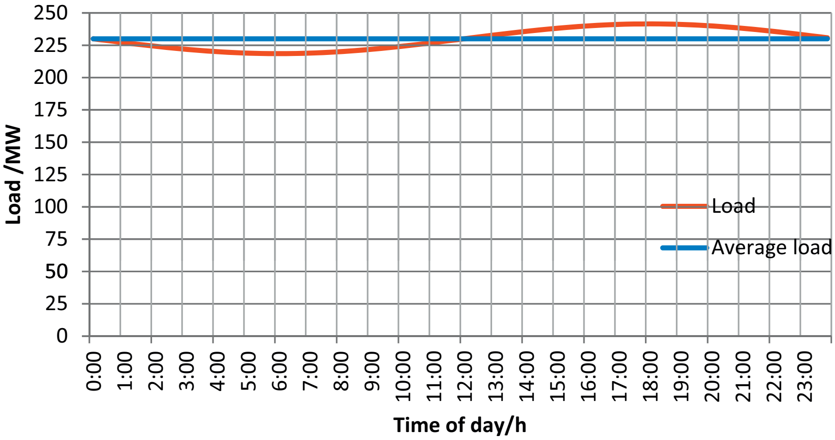


Figure 41. Modeled daily load curve for electricity of an industrial park.

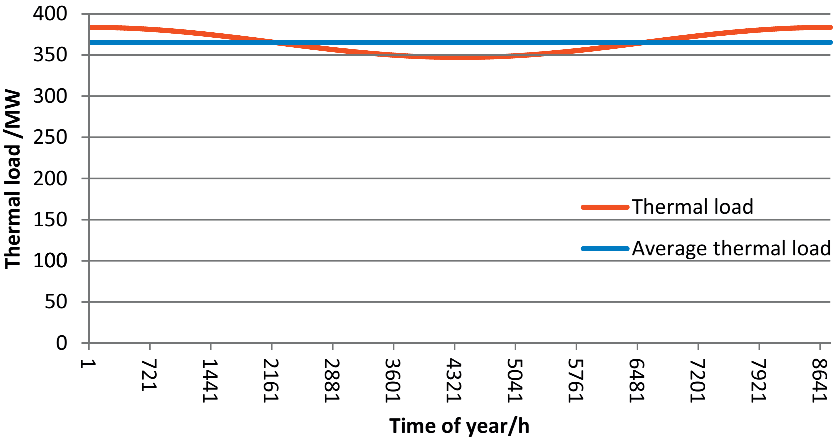


Figure 42. Modeled heat-load profile of an industrial park over the course of one year (8760 h).

5.2.3 Adaptation of an Industrial Site to Renewable Energy

Generally, industrial sites are fully integrated into the existing power grids. Regardless of the local supply capacity, ample supply of the facilities must be ensured. From the perspective of an industrial park operator, the security of supply by means of internal or external capacities is primarily a question of economic optimization and not an exercise in self-sufficiency. The complete integration into the existing energy infrastructure is both a necessity and an opportunity to reduce costs.

Supplying an industrial site on the basis of renewable energy is a fundamental challenge in the context of the energy transition if Germany is to remain an attractive location for energy-intensive industries. The high thermal energy requirements of an industrial site may continue to be most efficiently ensured by CHP plants. As fuel based on renewable energy, purified biogas in natural gas quality (biomethane) can be used.

Assuming that the combined-cycle power plants used have an overall efficiency of 90 % (30 % power, 60 % heat), the supply of a heat demand of 3200 GWh requires the provision of a total of 530 million m^3 biomethane, whereby also 1600 GWh a^{-1} of power is generated. This rough calculation was carried out with a lower calorific value for biomethane of 10 kWh m^{-3}. Furthermore, an overall efficiency (electricity and heat) of 90 % was considered. According to data of the Federal Network Agency (*Bundesnetzagentur*), in 2013 a total of 144 biogas plants in Germany injected 520 million m^3 of purified biomethane into the natural gas grid [124], i.e., about the same amount as mentioned above, at an average cost of 7.5 ct kWh^{-1}.

Thus, the entire biogas production in Germany would currently be needed to cover the heat demand and the majority of the electricity needs of a single industrial site. In addition, the price difference between biogas and fossil natural gas, with an average natural gas price of 3.76 ct kWh^{-1} (2013) is incurred [21]. This results in additional fuel costs of 195 million € compared to cogeneration of power based solely on natural gas, which is currently compensated by the subsidy for biogas producers.

Other options for securing the heat supply in cogeneration plants via renewable energy are the use of water treatment sludge or alternative fuels (from the treatment of industrial and municipal waste).

In the scenario above, an additional 400 GWh a^{-1} of electricity must still be provided from renewable sources. One option are hydroelectric power plants which could ensure a continuous supply. In 2013, the German run-of-river power plants contributed a total of around 16 TWh to the electricity supply [125] and, as base load-capable plants, are able to meet the demand. An example is the hydropower plant at the barrage Griesheim in Frankfurt, which produces 35 GWh of electricity annually at a drop height of 4.5 m and a width of the weir of 40 m [126].

Supply from offshore wind farms would also be possible. For comparison, the wind farm alpha ventus (investment costs: 250 million €) generates an annual average of around 250 GWh of electricity with a nominal output of 60 MW [127]. Therefore, purely mathematically, 1.6 offshore wind farms of the size of alpha ventus would be needed to compensate for the missing amount of electricity. Onshore wind farms may have higher nominal output, but only about half (depending on location) of the full-load hours achieved by offshore wind farms. Since wind energy is not base load compatible, adequate capacities would have to be provided in addition, e.g., by electricity storage.

Power storage facilities of this magnitude are not currently available. One possibility would be the use of power-to-gas processes to provide the necessary storage capacity in the form of methane. For the actual electricity supply also gas turbines would have to be available with a capacity of around 50 MW. In this case, at an assumed efficiency of 25 % (electricity to hydrogen to electricity), for the entire process a total of 1600 GWh a^{-1}, i.e., the equivalent of 6.4 alpha ventus offshore wind farms, would have to be used plus the entire power-to-gas infrastructure.

This thought experiment can be extended. If the heat supply (via power to heat) is switched to electricity, under the simplified assumption of complete conversion, a total electricity demand of 4800 GWh a^{-1} results. Under the simplified assumption of complete conversion of electricity to heat, 19.2 wind farms would have to supply the industrial park. Due to the uncertain availability of wind energy, corresponding capacities for heat (400 MW) and electricity (250 MW) generation and storage would have to be available to ensure a secure energy supply.

5.3 Seasonal Balancing Storage through Power to Gas

A power supply dominated by renewable energy requires a further, massive expansion of installed wind power and photovoltaic technologies. This leads to high temporary surpluses of electric power, whose possible alternative uses are being intensively discussed. The following explanations do not claim to fully describe the subject, which is the preserve of detailed studies. Instead, a sense of the magnitude of the challenge can be conveyed and various potential usage options for surplus power, especially the shift in the area of mobility, are outlined.

In addition to the domestic storage of photovoltaic power to increase self-consumption, a further need for energy storage arises from the increasing proportion of volatile renewable energy sources. Due to weather-related fluctuations in electricity generation, more electricity than is needed can be produced during times of strong wind or sunlight.

To identify appropriate storage technologies and usage paths, an estimate of the generated excess capacity must first be specified. To do so, the residual load produced by the electrical load minus the fluctuating feeding of renewable energy and 'must-run capacity' is calculated. Must-run capacities comprise all other capacities that produce electricity, but cannot be regulated according to the power requirements of a given day; they must always be available and include power plants to maintain network stability, hydroelectric power plants, heat-controlled CHP systems and inflexible conventional power plants.

Despite efforts to increase efficiency, electrical consumption, based on 2012 figures, has remained constant. Thereby, the increasing degree of electrification must be considered. To calculate the future input, current feed-in profiles of photovoltaics and wind turbines are used and scaled according to their expending development. The onshore wind-energy input calculation takes into account an additional increase in the full-load hours that results from improved rotor technology and higher hub heights. To determine the offshore wind energy input, wind data from the 90 m height research platform FINO 1 [128] can be used and be projected as generated power [14]. The resulting full-load hours (4250 h a^{-1}) are in the upper range of those of previously operated offshore wind farms [129].

Therefore, the expansion corridors of 2.5 GW, anchored in the current EEG, are used for photovoltaics and onshore wind turbines [18]. For offshore wind power, expansion targets of 6.5 and 15 GW for 2020 and 2030 are assumed, respectively. Thereafter, a further scale-up of 1 GW a^{-1} is expected.

For the current minimum must-run capacity of 20 to 25 GW, inflexible conventional power plants make the primary contribution. The future minimum active power generation of conventional power plants necessary to maintain voltage is estimated at 4 to 20 GW, with 8 to 25 GW [130] required to regulate the system balance. The current value is expected to be reduced by increased flexibilization of existing power plants, improved system services such as through the provision of balanced power and reactive power by renewable energy, as well as more flexible CHP plants with thermal storage. For the following calculation a must-run capacity of 10 GW is assumed, largely due to cogeneration and hydroelectric power plants.

In addition to excess capacity, the storage demand is crucial to identify suitable storage technologies. From their ratio, an average number of annual turnovers is calculated and thus a distinction is made between short- and long-term storage. For this purpose, consumption must also be calculated from the residual load in addition to the input rate. Two alternatives exist: In the first case, it is assumed that the stored energy is used for reconversion during periods with positive residual load. In the second case, an external consumer is assumed that constantly requires the same power throughout the year, which corresponds to the exact amount of energy supplied. The latter variant incorporates the chemical storage and subsequent use. To estimate the storage requirements in a technologically neutral manner, an ideal storage unit with charge and discharge efficiencies of 100 % is used.

Tab. 14 shows the development of electrical surplus energy and storage requirements under the given conditions. Clearly, the amount of excess energy will already reach significant levels from 2030 onwards (32 TWh) and will increase to greater than 200 TWh by 2050. The required amount of storage is already in the order of TWh from 2030 on, meaning that these requirements can no longer be met by pumped hydro storage power plants. The demanding storage requirements have seasonal characteristics, and were necessitated in particular by periods

Table 14. Excess capacity for future energy scenarios at a must-run capacity of 10 GW.

	2020	2030	2040	2050
Installed PV power [GW]	53	78	103	128
Installed onshore power [GW]	51	76	101	126
Installed offshore power [GW]	6.5	15	25	35
Full-load hours PV [h a^{-1}]	982	982	982	982
Full-load hours onshore wind turbine[a)] [h a^{-1}]	1700	1800	1900	2000
Full-load hours offshore wind turbine [h a^{-1}]	4250	4250	4250	4250
Peak excess power [GW]	21.2	55.1	91.1	125.0
Excess energy [TWh][b)]	2.5	32.0	103.0	203.1
Storage requirements (reconversion) [TWh]	0.4	6.3	17.0[c)]	11.8[c)]
Storage requirements (const. consumers) [TWh]	0.9	6.1	12.3	17.8

[a)] The increase in full-load hours for onshore wind energy is based on the assumptions that the development of plant technology permits greater utilization of low wind periods, that the average hub height will increase and thereby increases the yield of the plant, and that repowering modernizes old plants. [b)] The estimates for the expected surplus amounts of energy vary widely in the literature; see also [17] and [20]. [c)] For these scenarios the excess amount exceeds the need for reconversion. The specified storage requirement is part of the total storage requirement for the reconversion.

of strong wind, which occur mainly in the winter months and may persist for several days to weeks. In the case of storage for reconversion, a completely renewable supply is already projected to have been achieved before 2040, except for the fossil-fuel fraction of must-run power, such that the remaining excess energy will need to be used elsewhere.

This overproduction may be partially discharged into neighboring countries, but this is limited by respective grid capacities. In addition, the expansion of renewable energy is also taking place in neighboring countries, and thus this is not a long-term solution. Due to the periods of strong wind that occur especially in winter, stretches of several weeks of excess current may need to be contended with, and therefore, a simple load shift is not sufficient.

In the following, amongst all possible energy storage solutions, the focus is on those using chemical storage systems, since these provide required storage capacities for the quantities foreseen and are suitable for seasonal storage. Surplus power is converted to hydrogen by electrolysis. Starting from hydrogen, the economic potential depends on the use or further conversion.

Table 15. Technical and economic parameters used.

Parameter	Value
Technical parameters	
Efficiency, electrolysis [%]	70
Efficiency, methanation [%]	80
Efficiency, CCPP [%]	55
Compression, hydrogen [kWh $kg^{-1}{}_{H2}$]	3.2
Economic parameter	
Remuneration of surplus power [ct $kWh^{-1}{}_{el}$]	6
Grid usage charges, electricity to electrolyzer [ct $kWh^{-1}{}_{el}$]	1.37
Investment costs, electrolyzer [€ $kW^{-1}{}_{el}$]	500
Investment costs, methanation [€ $kW^{-1}{}_{CH4}$]	600
Investment costs [€ $kW^{-1}{}_{el}$]	750
Investment costs per cavern (750 000 m^3 volume) [million €]	30
Investment costs, H_2 pipeline network for 9860 gas stations [Mrd. €]	23
Investment costs gas stations (1500 $kg_{H2}d^{-1}$) [€ gas $station^{-1}$]	2 000 000
Electricity costs for compression [ct $kWh^{-1}{}_{el}$]	15
Annual discount rate [%]	8
Costs of operation and maintenance [% $a^{-1}{}_{investment}$]	3
Depreciation period, conversion plants [a]	10
Depreciation period, distribution grid [a]	20
Depreciation period, transmission grid and storage [a]	40

5.3.1 Design of Electrolysis Plants

Depending on the individual state of development, different load-duration curves result (Fig. 43). With increasing expansion not only the amount of the excess energy increases, but the distribution will also shift towards higher numbers of full-load hours.

For the following design and cost calculations, 2050 is taken as the reference year. The underlying cost data and assumptions are listed in Tab. 15. As these suggest, the remuneration of the excess electricity is particularly noteworthy. Despite temporary overproduction, power is assigned a remunerable value, which here is set to 6 ct kWh^{-1}. Thus, it is avoided that resulting electricity production costs, e.g., due to the EEG levy, are being passed on to electricity consumers and are instead included in the product as a cost component.

Depending on the scenarios considered, different cost calculations must be performed. Below, four different cases are investigated:

- Supply of hydrogen from renewable sources to the natural gas grid
- Supply of renewable sources of methane to the natural gas grid
- Central storage and reconversion of hydrogen from renewable sources
- Use of hydrogen from renewable sources in the transport sector with its own hydrogen infrastructure

These are analyzed in terms of their costs. Subsequently, a classification of these costs in comparison to the respective competitors is undertaken via an evaluation of the scenarios in terms of their economic potential.

All scenarios have in common that in the dimensioning of the electrolysis plant, the full-load hours increase with increasing installed capacity, while the fraction of unused excess energy decreases

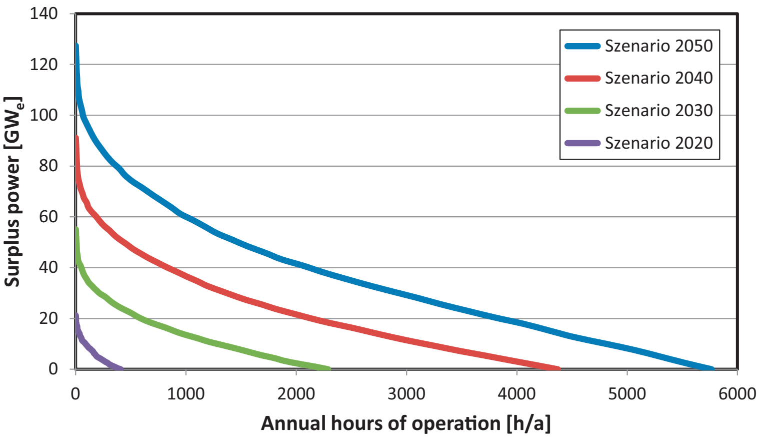


Figure 43. Annual performance curve of the expected surplus power for future energy scenarios.

(Fig. 44). This is especially important if an economic evaluation is performed in which the cost of the down-regulated energy is also taken into account. Notably, in the evaluation of the down-regulated energy, the power peaks, which occur only rarely, have only little energy content. An electrolyzer design that maximizes surplus power would consequently lead to a lesser degree of utilization of the electrolyzer and thus to significantly increased costs.

5.3.2 Scenario 1: Feeding of Renewably Generated Hydrogen into the Gas Grid

The use of the existing natural gas infrastructure for the transport and use of hydrogen from renewable sources allows rapid implementation of this power-to-gas concept since, in addition to the electrolyzer and its peripherals no additional components are needed. Restrictions arising from a maximum H_2 concentration in the gas (see Sect. 4.2.5) are not considered here.

Fig. 45 shows the hydrogen production costs as a function of the electrolyzer is installed power. Due to the decreasing workload, the specific H_2 generation costs increase from 12.7 cents $kWh^{-1}{}_{H2}$ to 18.7 ct $kWh^{-1}{}_{H2}$ at maximum installed power (equivalent to 4.2 or 6.2 € $kg^{-1}{}_{H2}$). Of these costs, approximately 10.5 ct $kWh^{-1}{}_{H2}$ is attributable to energy costs, and the remainder to the electrolysis plant itself. If, in addition to the purely economic point of view, the remuneration of the down-regulated amount of energy is also taken into account, there is an economic optimum at an installed electrolysis capacity of 59 GW_{el}.

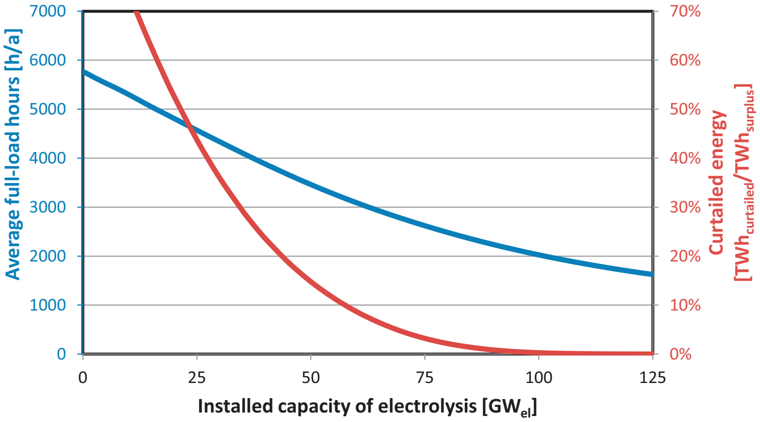


Figure 44. Full-load hours of the electrolyzer in relation to the downregulated energy depending on the performance of the installed electrolyzer.

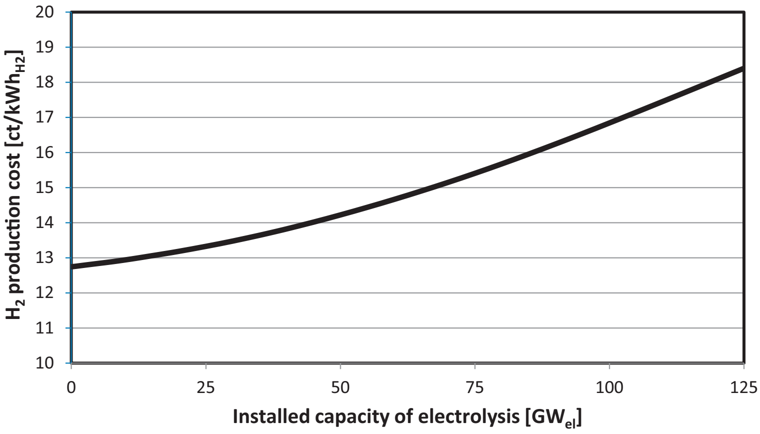


Figure 45. Production costs of H_2 for feeding into the natural gas grid.

To estimate the economic potential of hydrogen feed into the gas grid, the hydrogen production costs must be compared with those of the competitor, in this case natural gas. The price for large industrial customers in recent years ranged from 3.1 to 4.1 ct $kWh^{-1}{}_{CH4}$ without VAT [131]. This means that, neglecting the accumulating network usage charges, hydrogen is currently more expensive than the competing natural gas by at least a factor of three. Consequently, cost effectiveness can only be achieved by subsidization of hydrogen or by a higher taxation of natural gas.

5.3.3 Scenario 2: The Feeding of Renewably Generated Methane into the Gas Grid

With the conversion of regeneratively produced hydrogen to methane, all feed restrictions are eliminated, so that the natural gas network including its storage facilities can be used to its full extent. This is offset by the need for a source of CO_2, additional investments for a methanation plant, and the efficiency losses associated with the process. The supply of the carbon dioxide imposes costs depending on its source and mode of transport; with CO_2 captured from conventional power plants costs of 25 to 55 € $t^{-1}{}_{CO2}$ incur [132], when captured from air, potentially multiples thereof. At the same time, however, there is also the option of reimbursing unused carbon dioxide. To determine the impact of the CO_2 price, three hypothetical cases are discussed: CO_2 costs of 100 € $t^{-1}{}_{CO2}$, cost-neutral CO_2 and CO_2 remuneration of 100 € $t^{-1}{}_{CO2}$. In addition, the methanation plant is dimensioned according to the maximum hydrogen production of the electrolyzer, so that any buffer for the hydrogen is omitted.

In the case of methane production, the dependence of the production costs on the installed electrolysis capacity is higher than for hydrogen, since the capital costs, arising from additional methanation, increase. For an installed electrolysis capacity of 60 GW, the total costs of 21.8 ct $kWh^{-1}{}_{CH4}$ are composed of 13.2 ct $kWh^{-1}{}_{CH4}$ for the energy costs, 5.1 ct $kWh^{-1}{}_{CH4}$ for electrolyzers, and 3.5 ct $kWh^{-1}{}_{CH4}$ for the methanation plant (Fig. 46). The increased energy costs arise from the lower overall efficiency of the process chain. The CO_2 costs and compensation lead to a change in the basic costs of ± 2 ct $kWh^{-1}{}_{CH4}$ and thus only have little impact on prices.

Similar to the supply of hydrogen from renewable sources, the costs of synthetically produced natural gas must also be compared to the price of conven-

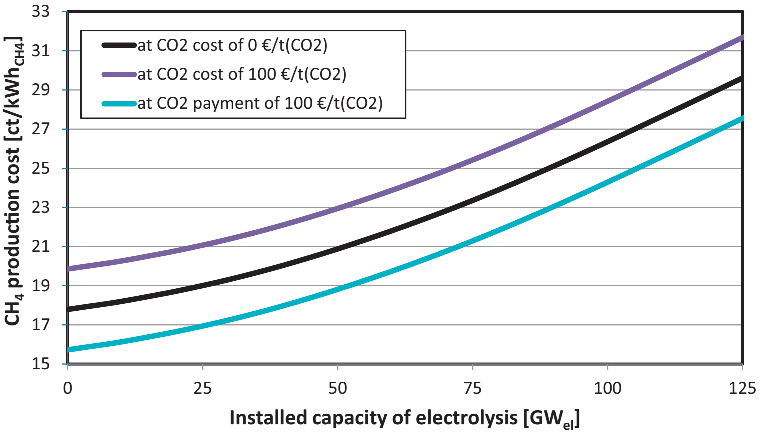


Figure 46. Production costs of CH_4 for feeding into the natural gas grid.

tional natural gas. Here, the cost ratio with a factor of > 4.5 is even more substantial, making the supply of renewable natural gas technically feasible, but not economically competitive.

5.3.4 Scenario 3: Central Storage and Reconversion of Hydrogen from Renewable Resources

If the power-to-gas technology is used as a storage medium for reconversion, the use of a reconversion infrastructure in addition to the natural gas infrastructure may also be worthwhile, since unnecessary conversion steps and investments are avoided. Such infrastructure includes, beside the electrolyzers, the salt caverns and reconversion, which in this case means combined-cycle power plants. Their dimensioning is of particular importance here. If the installed combined-cycle gas turbine (CCGT) capacity is designed for the maximum required reconversion performance, the fixed costs of this power plant would be disproportionately high, especially with poor electrolyzer performance due to low degree of utilization. Thereby, the reconversion costs would unnecessarily increase, as in these cases, other power plants are needed to cover the residual load. Only with complete coverage of the required residual load by H_2 reconversion can the required reconversion benefits be completely secured. Therefore, the H_2 gas-and-steam power plants are dimensioned so that the electricity production costs for reconversion are minimal.

Fig. 47 shows the total electricity production costs as a function of the installed electrolyzer performance. From an installed capacity of 37 GW upwards, the total residual power demand is covered by reconversion of hydrogen. The price of 34.0 ct kWh_{el}^{-1} is composed of 19.1 ct kWh_{el}^{-1} for the electricity, 5.8 ct kWh_{el}^{-1} for electrolysis, 0.8 ct kWh_{el}^{-1} for cavern storage, and 8.3 ct kWh_{el}^{-1} for combined-cycle-power plants. The sharp increase in reconversion costs is caused by both the lower degree of utilization of the electrolyzers and the combined-cycle power plants.

The full costs of a natural gas-fired combined-cycle power plant is about 8 ct kWh^{-1}_{el} at a CO_2 emission certificate price of 25 € t^{-1}_{CO2} [133]. In contrast, electricity generation costs for reconversion are four times as high. Even if the related power were not remunerated, the remaining electricity generation costs of 14.8 cents kWh^{-1}_{el} under the given conditions would not be competitive with today's alternative power generation options. However, in the future, the value of a reconversion option could allow higher electricity prices than is currently economically feasible.

5.3.5 Scenario 4: Use of Hydrogen from Renewable Resources in the Transport Sector with Its Own Hydrogen Infrastructure

Another application of the hydrogen generated from renewable sources is its use in the transport sector. In particular, fuel-cell vehicles require pure hydrogen; however they do not produce pollutants or carbon dioxide. Therefore, the use of hydrogen from renewable sources in fuel-cell vehicles will contribute to CO_2-free transport.

However, this requires a comprehensive hydrogen infrastructure consisting of electrolyzers, salt caverns, a transmission and distribution pipeline network as well as hydrogen filling stations. Analogous to the reconversion scenario, the required cavern storage size is determined by the filling level. Since in this paper a separate pipeline system is not designed, the calculations of Krieg [134] are used. To ensure nationwide coverage, the transmission network is fully developed, while the numbers of hydrogen refueling stations and distribution networks required therefore are scaled in proportion to the amount of hydrogen.

The fixed costs due to expansion of the transmission pipeline network lead to an exponential increase in H_2 total cost at low amounts of hydrogen (Fig. 48). With increasing electrolysis performance and a concomitantly increasing amount of hydrogen produced, the influence of the fixed costs decreases,

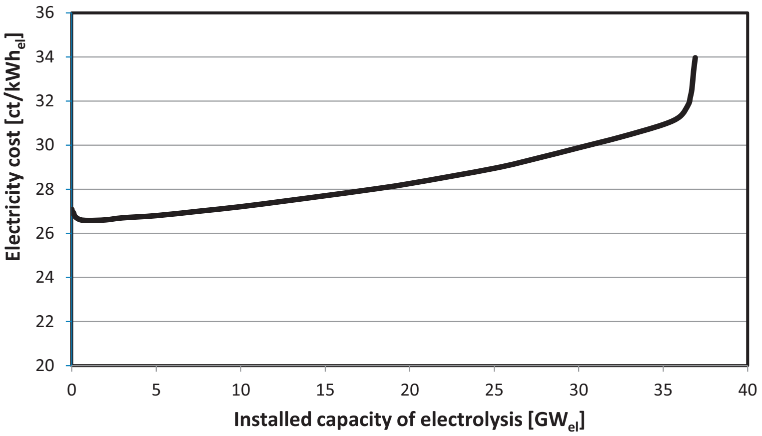


Figure 47. Production costs of electricity for reconversion of renewable hydrogen.

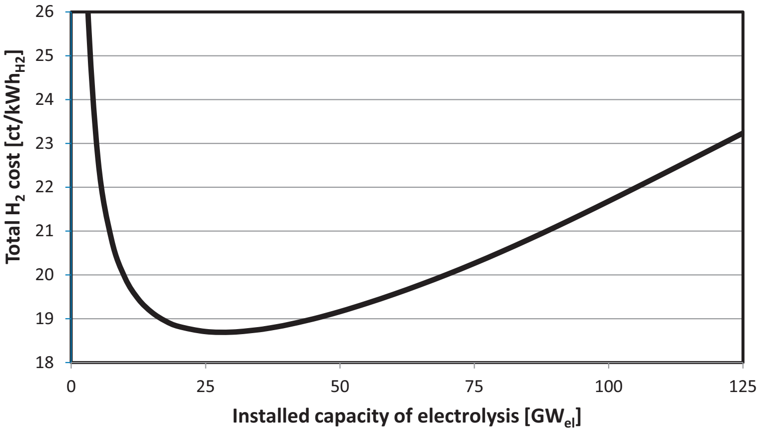


Figure 48. Total cost of H_2 when used in transport.

but so does the degree of utilization of electrolysis plants. Accordingly, a minimum cost arises at 27 GW$_{el}$ installed electrolysis performance. The hydrogen costs of 18.7 ct kWh$^{-1}{}_{H2}$ reflect 64 % electricity costs, which are also applied for compression, 15 % electrolyzer costs, and 21 % infrastructure costs, which include storage facilities, service stations, and the pipeline network. The hydrogen quantity of 2.54 million t generated by this point would be enough to supply 16.9 million fuel-cell vehicles assuming a consumption of 1 kg$_{H2}$/100 km and an annual distance travelled of 15 000 km.

When comparing the costs of hydrogen with those of other fuels, the efficiency of the means of transport must also be considered. With 1 kg$_{H2}$/100 km, the consumption of the Mercedes-Benz F-Cell is equivalent to about 3.3 L diesel /100 km or 3.7 L gasoline/100 km. This corresponds approximately to half the specific energy consumption of a comparable car with a combustion engine [135]. Automobile manufacturers expect to reduce fuel consumption even further, proposing values of around 0.7 kg$_{H2}$/100 km. Therefore, for a recent gasoline net price of 67.85 ct L^{-1} without taxes in Rotterdam [136], corresponding to 8.0 cents kWh^{-1}, the allowable price of hydrogen to achieve cost parity is between 16.0 ct kWh^{-1} and 22.9 ct kWh^{-1}. Thus, hydrogen production costs would be in a competitive range to conventional fuels.

5.3.6 Comparison of Scenarios and Conclusion

The production of hydrogen by electrolysis using temporary surplus power would enable the storage of energy volumes on a scale of tens of TWh, even over seasonal periods. The calculation of excess energy at constant growth of renewable energy has shown that this might already be needed from 2030 on. The efficiency of this storage option depends to a considerable extent on the subsequent use of the hydrogen produced. Therefore, the options of central reconversion, H_2 or CH_4 as substitute for natural gas, and hydrogen as a fuel for the transport sector were further examined. To enable comparability with each other, the installed electrolysis power is adapted to the various options for the scenario in 2050 such that the fraction of regulated excess energy relative to all excess energy does not exceed 5 %. This is achieved with an electrolysis performance of 69 GW. An exception is central reconversion, for which the electrolysis is dimensioned at 37 GW, since above this level the amount of hydrogen produced is sufficient for full coverage of the residual load requirements.

As a result, the costs of feeding into the natural gas grid range from 15.1 ct kWh$^{-1}{}_{H2}$ to 22.7 ct kWh$^{-1}{}_{CH4}$. Thus, compared to the current natural gas price for industrial consumers of about 4 ct kWh$^{-1}{}_{CH4}$, the costs of gas from renewable sources are therefore higher by a factor of four to six. Even a remuneration of 100 € t$^{-1}{}_{CO2}$ for the required carbon dioxide to produce the renewable methane would only lead to a cost reduction of 2 ct kWh$^{-1}{}_{CH4}$ (Fig. 49).

The option of reconversion makes the total cost of reconverted hydrogen 34 ct kWh$^{-1}{}_{el}$. Compared to the full cost of conventionally generated electricity, this value is more than four times as high. The high costs are in particular a product of the low overall efficiency of the process chain of < 40 %.

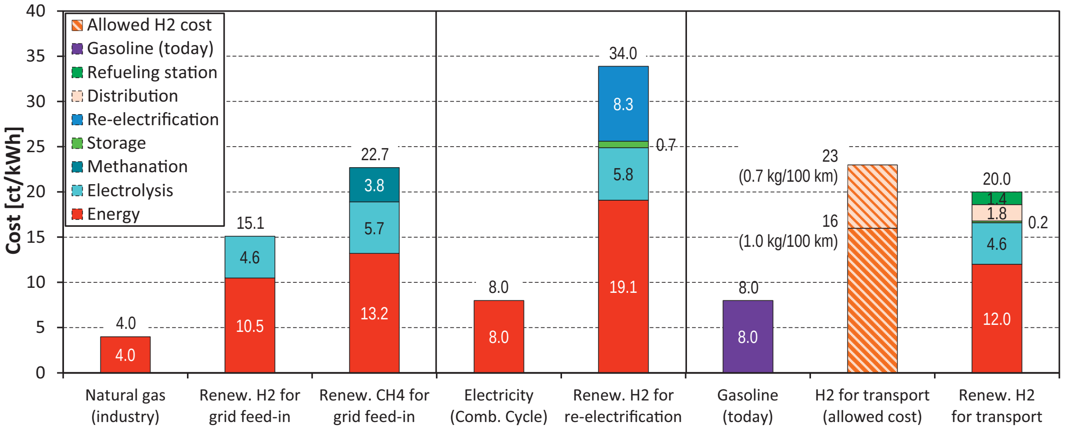


Figure 49. Cost comparison of different power-to-gas options depending on the purpose of use for scenario 2050 with an installed capacity of 69 GW electrolysis or 37 GW in the case of H_2 reconversion.

In contrast, the use of hydrogen as a fuel in the transport sector allows almost cost-covering remuneration. This is, in particular, due to the efficiencies introduced by the powertrain of fuel-cell vehicles compared to that of conventional vehicles with internal combustion engines. The comparison shows that the use of hydrogen generated from renewable sources as a transport fuel is the favorable option from today's perspective, since under the given conditions it has the potential to be economically realized.

6 Conclusion and Outlook

Energy storage technologies are available for the most diverse applications. The requirements of the application areas are so different that a broad range of storage technologies is needed to most efficiently meet the requirements. Therefore, future developments should be designed as openly as possible.

Thereby, energy storages should be regarded as a system whose various functions (loading, storing, discharging) can be performed by different components and in various forms of energy. The resulting conversion losses must be assessed relative to the gain in flexibility.

In addition to pure energy storage, especially the use of chemical energy storage allows cross-linking of various strands within the energy system. The currently discussed chemical storage options all produce substances that have already established alternatives, including industrial applications and supply pathways, which define the economic conditions for operation of the storage option.

On the other hand, via power-to-X technologies, chemical energy storage also allows coupling of renewable energy from the electricity sector to those areas of the energy sector that currently have few alternatives to fossil fuels (e.g., heating, mobility, and energy-intensive industrial production). This could reduce the dependence on imports of conventional energy sources.

An isolated view of a storage system is in danger of ignoring synergies that result from the cross-linking options. Only a systemic view can be a sufficiently robust basis for evaluation.

On the one hand, the criteria should include technology-specific parameters for the possible applications and operations, such as efficiency, service life, and economic costs. On the other hand, they should also address systemic parameters such as existing infrastructure, established value chains and markets as well as issues of social acceptance, gain in energy security or flexibility, and economic costs.

The current energy system is subject to fundamental transformation due to the increasing contribution of renewable energy, whereby energy storage technologies are becoming increasingly important. The existing technologies satisfy the demand in the current state of the energy system, but are not sufficient to meet the future challenge for several reasons. The research and development of new storage technologies and demonstration of the associated process chains on an industrially relevant scale are therefore essential with respect to future changes in the energy system.

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Abbreviations

CEPS	Central European Pipeline System
CHP	combined heat and power
CNG	compressed natural gas
CSP	concentrated solar power
EEG	German Renewable Energy Sources Act
ETL	emissions-to-liquid
ETS	Emissions Trading Scheme
FT	Fischer-Tropsch
HBI	hot briquetted iron
HHV	higher heating value
LHV	lower heating value
LOHC	liquid organic hydrogen carrier
MTA	methanol-to-aromatics
MTO	methanol-to-olefins
MTP	methanol-to-propylene
PCP	primary control power
PEM	proton-exchange membrane
PTC	power-to-chemicals
PTG	power-to-gas
PTH	power-to-heat
PTL	power-to-liquid
SOEC	solid oxide electrolyzer cell
SOFC	solid oxide fuel cell
SRL	secondary control power
UPS	uninterruptible power supply
VRFB	vanadium redox flow batteries

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