Energy storage as an essential part of sustainable energy systems

A review on applied energy storage technologies

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Abstract

Energy supply is an intricate task that provides a reliable energy service to consumers throughout the year. Import dependencies, seasonal differences in energy supply and use, and daily fluctuations in consumption require a sophisticated management of energy resources and conversion, or energy distribution and resource intermittency in order to guarantee continuous energy services throughout all sectors. *Therein, energy storage plays a critical role.* Energy storage balances the daily fluctuations and seasonal differences of energy resource availability, which results from physical, economical or geo-political constraints. A strongly variable energy demand through day and night also requires energy to be stored in adequate amounts. In particular, short- and mid-term storage levels out or buffers energy output gaps or overflows. Energy is mostly stored in between conversion steps from primary to secondary energy and secondary to final energy. Often rechargeable systems are used to refill the storage capacity when energy demand is low and energy services are not needed.

Primary storage such as large crude oil and natural gas storage tanks are essential for the functioning of a country's energy system. Storage of water in reservoirs behind dams is valuable for selling hydropower electricity at the right time or in seasons of increased demand. Secondary or final storage systems, for instance in tanks or in batteries**,** are crucial for emergency situations, uninterrupted industrial production, long-distance mobility or to secure energy services at home.

Storage systems are engineered to hold adequate amounts of mechanical, thermo-physical, electro-chemical or chemical energy for prolonged periods of time. Energy storage systems should be quickly chargeable and should have a large energy storage capacity**,** but at the same time should also have high rates of recovery and high yields of energy regain.

Final energy in factories or households is often stored in tanks as chemical energy in the form of heating oil or natural gas. Thermo-physical energy in the form of steam, hot or cold water, or thermo-oils is also used. For some special applications or for safety reasons energy may be stored electrochemically in batteries or physically in the form of pressurized air. Other storage systems are related to electricity and apply mechanical storage in the form of spinning turbines or flywheels, physical storage in the form of water in reservoirs in highland terrains, or electrostatic storage in super-capacitors.

Research is extensive in the area of energy storage since an increase of new renewable energy technologies such as wind and solar is expected to increase fluctuations and deviations from grid parameters**.** These need too be balanced out using reserve power capacities, grid level power storage capabilities, distributed generation units connected to the grid, and possibly appropriate new grid architectures.

A. Introduction

Several different types of energy storage systems are used for primary, secondary, and final energy. Primary energy is predominantly stored chemically in oil or gas tanks, or in piles of specific energy carriers like biomass or coal. Secondary and final storage involves silos or piles of briquettes or biomass chips, or storage tanks for refined petroleum oils, fuels and gases. The conversion of these forms of energy into useful end-use energy including electricity provides for immediate energy services. If demand or system status changes, useful energy can also be stored using mechanical or physical storage systems, thermo-physical or thermo-chemical systems, electrochemical and electrostatic systems, or chemical storage systems. The proper functioning of an energy market is dependent on the available market chain, which consists of supply, storage and demand. Storage concepts must be well developed for an appropriate incorporation of storage technology into energy systems. For instance, imbalances in a domestic energy system for heat, gas and electricity can result in a country's increasing dependence on foreign gas- and oil companies and expensive trans-boundary high-voltage electricity transmission lines. The development of inexpensive storage options promise to cope with imbalances between demand and capacity, and variable prices in energy markets. An uninterrupted availability of clean energy products at the marketplace at a price that is affordable for both private and industrial consumers is important for the well-being of all citizens.

Energy systems rapidly change under the influence of energy policies. For instance, the ongoing liberalization or deregulation of energy markets could make small-scale and large-scale storage capabilities increasingly beneficial because of the emerging competition in the energy market. Increasing oil prices however reveal structural weaknesses in energy supply systems with the increasing energy dependence on oil, which still plays a major role in fuel consumption. Strategic petroleum reserves are an important regulatory aspect of energy supply systems in many countries. These address compulsory storage ratios negotiated between importing companies and the government. Adequate storage facilities must be available not only for crude oil but also for natural gas, which is expected to largely substitute oil in the near future.

With electricity, new renewable energy technologies such as wind and solar increase variations in the grid and therefore must by integrated properly into the existing electricity system. This involves local storage of electricity, which may require, among other things, installation of grid level power storage capabilities.

At the same time, industrial and commercial customers increasingly demand power quality and reliability, and a market is developing for "premium power" and customers dependent on properly functioning microprocessor systems. In general, the spread of information technology brings new requirements for the transmission and distribution of electricity.

Uncertainties in grid reliabilities shift the emphasis in energy storage from producers to distributors in order to guarantee energy service. Distributed power generation and storage interconnected with the distribution grid can provide the needed power quality. Besides energy supply reliability, incentives for energy storage include the moderation of increasingly volatile energy prices. Real time pricing in liberalized energy markets is expected to result in additional local storage within buildings and "intelligent" household appliances.

In summary**,** the development of storage systems can diminish dependency on oil and natural gas imports in the short to mid-term, ensure power quality, reduce energy price volatility, and, for electricity, help to integrate intermittent renewable resources into the grid. Failure to develop adequate storage measures along with energy systems, for instance new distribution systems, will pose a threat to the quality of energy services, possibly leading to higher future costs for infrastructure and energy services.

Although storage can improve the capacity and service of energy systems, according to the laws of thermodynamics, all storage systems are accompanied by a loss in efficiency. On the other hand, some of the loss can be regained using optimized end-use technologies and control devices, which also allow energy consumers to time energy purchases and shift from high to low rate periods.

To achieve the full potential of energy systems, both independent and grid-based power distribution systems rely on the availability of different storage technologies. These include, for instance, safe on-vehicle storage and infrastructure components to assure fuel availability at filling stations, which efficiently satisfy on-demand mobility. Other examples are new hybrid systems, which combine micro-turbines, photovoltaic panels or fuel cells for diverse industrial, commercial or residential applications. These custom power systems need to be electronically controlled within a complex grid containing multiple generating units. It requires additional storage systems such as batteries, super-conducting magnetic energy storage (SMES), and flywheel energy storage for power quality and reliability (Yeager et al. 1998). In both small uninterruptible power supply (UPS) systems for personal computers and in large pumped storage projects, energy storage will increase system reliability. At utility sites however, storage capabilities, which provide large-scale instantaneous response are required. In the future, underground storage technologies including SMES may be possible. Innovations to store hydrogen, recharging batteries or fuel cells, and facilitating high-temperature superconductivity have great potential to satisfy future heat and electricity storage requirements (Dresselhaus and Thomas 2001). In addition, new regulatory standards for efficiency and environmental compatibility request ever faster technical or technological innovations, such as heat-, corrosion-, abrasion- and impact-resistant materials; thermal and chemical functional materials for thermal storage, or insulation and cooling media.

B. Electricity Storage

Apart from the use of secondary batteries, electricity storage is predominantly carried out in form of mechanical energy. Large-scale electricity storage systems are suitable to balance differences between power supply and demand. Power must be deliverable in time frames of hours and days or months to balance seasonal changes. Large-scale electricity storage systems supply peak-load power using previously stored base-load electricity, or make it possible to integrate renewable energy technologies characterized by intermittent resource availability (e.g. solar and wind). In addition, large-scale electricity storage systems can supply regulating power for proper transmission and distribution of electricity through the grid. As part of the ancillary services, minimal power must be available – a few MW within seconds and ten times as much within minutes[1]. Sometimes such power levels must be sustained for hours. The following storage technologies are often used for large-scale electricity storage systems:

- Pumped storage hydropower reservoirs
- Compressed air energy storage
- Large-scale secondary batteries and large fuel cells

Other, smaller scale applications of electricity storage provide power for mobile systems or upgrade power quality and reliability (including emergency supply). Electricity storage for these applications has varied capacity and time-scale characteristics. The following technologies are applicable:

- Batteries and fuel cells
- Super-conducting (magnetic) energy storage (SMES)
- Super-capacitors and ultra-capacitors
- Flywheel energy storage

Batteries are often used in mobile applications and systems where reliability with low maintenance is important. Their release of power is instantaneous. Batteries can provide relatively prolonged power as compared to the other technologies. Capacitor and flywheel energy storage have rather different discharge characteristics, releasing high power in a short time frame. They are suitable for improving power quality, integration into emergency backup systems, and peaking in mobile systems when short-time power demand is high. Although still in the testing phase, fuel cells are suitable for providing power over long periods of time, and for continuous operation at various power ranges.

Both the capital costs of power and energy are important in evaluating the economics of storage systems. Typically the capital cost component of power is related to the output capacity, while the cost of energy deals with the storage capacity of the system (Table 1).

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[1] Pre-qualification Regulatory Energy, RWE Net AG, http://www.rwenet.de/

Table 1: Estimates of power capacity cost and energy capacity cost for different storage systems. Annual costs assume a discount rate of 9% and a 10-year life cycle.

Electricity storage system	Power capacity costs [US$/kW/a]	Energy capacity costs [US$/kWh/a]
Compressed air energy storage in tanks	120	100-1500
Underground compressed air energy storage	90	5-100
Large scale batteries	70	10-700
Pumped storage hydropower	50	3-90
Super-conducting magnetic energy storage	40	9-150
Flywheel energy storage	30	80-1200

Source: EESAT. "Proceedings of the International Conference of Electrical Energy Storage Systems: Applications and Technologies." *International conference Electrical Energy Storage Systems*, Chester, UK, 323.

1. Mechanical systems

a. Hydropower Storage

An important application of hydropower storage plants is to balance seasonal differences in electricity demand. The reservoir of the plant stores excess water from water-rich, lower-demand seasons, which is then used to generate electricity during water-poor, higher demand periods. Pumped-storage hydropower plants usually follow a different strategy. Extra water is pumped back up to the reservoir using base-load electricity when electricity demand is low, usually at night, and is then used for electricity generation during peak-load periods. Today, the increase of electricity generation from renewable energy sources such as wind and solar requires additional storage due to the intermittency of its generation.

i. Storage hydropower plants

Hydropower storage plants accumulate the natural inflow of water into reservoirs, i.e. dammed lakes, in the upper reaches of a river where steep inclines favor the utilization of the water heads between the reservoir intake and the powerhouse to generate electricity. This efficient storage of potential energy allows hydropower storage schemes a broader range of energy benefits than pure run-of-river schemes. Reservoirs at the upper watershed regulate the river downstream, which will typically flow more evenly throughout the year, and the run-of-river power generated downstream utilizes part of the same water used upstream for the hydropower storage plant. Reservoirs can provide a seasonal, annual or multi-annual storage capacity. Hydropower plants are used as a part of larger parks of hydropower schemes to follow demand along the load curves. It produces electricity preferentially during periods of higher load. The use of large storage volumes is often controversial because of considerable environmental impact including the issue of pumping water from catchment areas faraway from the natural catchment areas of the river in order to enhance inflow to the reservoir.

ii. Pumped storage hydropower

The most widespread large-scale electricity storage technology is pumped storage hydropower. A pumped storage plant uses two reservoirs; an upper storage basin providing the head to drive the hydropower turbines, and another to collect water back into the upper basin using surplus base-load electricity during off-peak hours. The stored energy is only utilized for electricity generation during daily peak-load. By definition, a pure pumped storage plant uses less than 5% of inflow from upper watersheds, and is therefore an energy system storage component, not a renewable energy source (IEA 2001). Using "green electricity," for instance from surplus wind power, to pump water back to reservoirs during periods of low demand and using the additional storage volume for grid regulation and balancing stochastic output are interesting scenarios for a future sustainable energy system. As the share of renewable energy grows, such a system will be well suited to cope with their intermittency of output, however its economic performance will always be strongly dependent on the price of the cheapest electricity produced by other plants and the variation in daily load.

Hydraulic turbines have a very high efficiency of more than 95% while pumps are less efficient. The result is a maximum efficiency of around 85% for pumped storage hydropower plants. The effective efficiency is determined by the roundtrip cycle efficiency, which calculates the cycle with the turbine operated both as a "generator " and as a "pump". Hence, designs of pumped storage are optimized for overall efficiency and dynamic response. The effective efficiency is between 65-70%, and for each kWh electricity produced, some 1.4 kWh of energy is necessary for pumping assuming the same architecture for both operation modes. Still, pumped storage is considered to be one of the most efficient ways to store and regain electricity.

Economic performance is highly dependent on the price of the cheapest electricity produced by other plants and the variation in daily load. The energy that can be extracted from a hydropower plant depends on both the volume of water available and the head of water that can be exploited. A pumped storage project will provide the most efficient and cheapest operation when it can provide a high water head and volume between its two reservoirs. This will allow the greatest amount of energy to be stored in the smallest volume of water resulting in smaller pumps and turbine, thus reducing capital costs.

Appropriate location, equipment and construction are particularly important in view of the high costs associated with pumped-storage systems. In general, pumped-storage sites with high heads and short water passages are more desirable (IEA 2001). It is therefore important to identify cost-effective sites with higher water head ranges, normally varying between 300 m and 800 m, and relatively steep topography. Shorter water passages will reduce the need for surge tanks to control transient flow conditions. With higher heads, smaller volumes of water provide the same level of energy storage, and smaller size water passages can be used for the same level of power generation.

The global pumped storage hydropower capacity is estimated at 82,800 MW. Capital costs are likely to be in line with those for a conventional project, i.e. between $1000/kW and $3000/kW. The payback time will depend on the difference in value of peak and off-peak power. Because of the possible significant environmental impact of these schemes, the availability of suitable sites in the future

will limit growth in pumped hydro capacity. Initial capital costs for construction will also increase due to environmental obligations. Even so, the role of pumped-storage plants is likely to increase in the longer term.

b. Flywheels

Today's flywheel energy storage systems can provide highly reliable, high-quality, uninterruptible electric power for communications networks, computers, the Internet, industrial manufacturing, commercial facilities, and distributed generation applications. Very heavy flywheel systems have been used for many years in electricity plants, and smaller systems are now under demonstration for mobile units.

The charging of a flywheel is based on putting heavy symmetrical circumferenctial masses, originally made of steel, into rotation. The masses can rotate at about 50,000 revolutions per minute almost without friction around a titanium axle using magnetic bearings. The rotating masses are used in conjunction with a dynamo to generate electricity on demand.

The higher the angular velocity of rotation (ω, radians per second) and the further away from the center the flywheel masses are placed, the more energy is stored, the relationship being $1/2 I\omega^2$, where I, the moment of inertia of the flywheel, is the product of the total masses M and the square of their mean distance r from the center. Since the centrifugal forces are equal to $M\omega^2 r = I\omega^2/r$, for a given flywheel diameter and thickness, higher stored energy requires stronger flywheel materials to withstand the rotational forces. For materials such as fused silica the specific energy stored in watt-hours per kilogram (Wh/kg) is more than 20 times better than steel-based flywheels and about 40 times better than lead-acid electric vehicle batteries (Table 2).

Table 2: Energy densities of storage media

Media	Wh/kg[a]
Hydrogen	38000
Gasoline	13000
Flywheel, fused silica	870
Flywheel, carbon fiber	215
Flywheel, steel	48
Lead-acid battery	25

[a] weight of motor and generator, and conversion efficiency not included

Source: Ristinen, R. A., and Kraushaar, J. J. (1999). *Energy and the Environment*, John Wiley & Sons, New York.

The latest modern flywheel energy storage systems make use of advanced composite materials and state-of-the-art active bearing technologies. Single flywheel units are typically 5kWh-100kWh and can be cascaded to achieve utility-scale power and energy ratings. Much larger systems are currently being developed in various research laboratories, particularly in Japan and the USA (Collinson 2001). Recently, a 2 kWh composite flywheel system was introduced and flywheels with increased power ranging up to 4 kWh should now be available. Plans include production of an 8 kWh model, which is to be followed by a 20 kWh unit. Medium-scale storage (0.1-10.0 MWh) still has some unsolved technological problems (Collinson 2001).

Several companies are experimenting with pairing micro-turbines with a fuel cell or flywheel system as a complete hybrid backup power system.
Ceramic superconducting materials could also be applied in flywheel energy storage. A small-scale application could for example be a flywheel running on frictionless bearings by means of magnetic fields that are generated by the superconducting materials.

i. Flywheels for vehicles

Electric buses or trains could use rapidly-rotating flywheels for energy storage instead of secondary batteries. Urban transit buses and military vehicles have used stored inertial energy as early as the 1970s. However, some impractical aspects, including a short range of only around 10 km have limited their applicability. Modern flywheels can store much more electricity than contemporary metal hydride or lead-acid batteries of similar weight or volume. Flywheels are environmentally friendly and have a much longer lifetime than electrochemical systems. Today's high performance materials enable the design of electric vehicles with flywheel systems that can be comparable to petroleum-powered vehicles. Similar acceleration, speed and range per unit weight of energy stored, including regenerative braking, are achieved.
Some hybrid vehicles use a flywheel for energy storage, and have shown similar performance to that of electric vehicles with supercapacitor or modern battery energy storage. Engine and flywheel sizing requirements must be analyzed to obtain the desired level of performance. One of the goals is to develop a zero-emission vehicle which combines hydrogen lean-burn spark-ignited engines with a high fuel economy or hydrogen fuel cells, both incorporating flywheels or supercapacitors as acceleration and braking energy recovery systems (Aceves and Smith 1996).

c. Compressed Air

In compressed air energy storage (CAES) air is compressed and stored under pressure. Release of the pressurized air is subsequently used to generate electricity, most efficiently in conjunction with a gas turbine. In a CAES plant compressed air is used to drive the compressor of the gas turbine, which makes up 50-60% of the total energy consumed by the gas turbine system (Collinson 2001). The most important part of the CAES plant is the storage facility for compressed air. Usually a man-made rock cavern, salt cavern, or porous rock, either created by water-bearing aquifers or as a result of oil and gas extraction, can be used. Aquifers in particular can be very attractive as storage media because the compressed air will displace water, setting up a constant pressure storage system. The pressure in the alternative systems will vary when adding or releasing air.
The largest CAES plant was 290 MW, which was built at Huntorf in Germany. This plant operated for 10 years with 90% availability and 99% reliability. Although the German utility decommissioned the plant, CAES technology was promoted in the latter half of the 1980s in the US. The Alabama Electric Co-operative built a 110 MW commercial project. The plant entered service in May 1991 and has since generated over 55 GWh during peak demand periods. The same year Italy tested a 25 MW installation. A 1050 MW project has apparently been proposed in the Donbass region, on the Russia-Ukraine border.
The annual investment costs for a CAES are estimated between \$90/kW/yr and \$120/kW/yr, i.e. uniform cash flow, depending on air storage type (EESAT 1998).

With a 9% discount rate and a 10-year life cycle, these correspond to necessary initial investments between \$580/kWe and \$770/kWe.

As with pumped storage capacity, the development of large-scale CAES is limited by the availability of suitable sites. As a result, current research is focused on the development of systems with man-made storage tanks.

2. Electro-chemical systems

The oldest and best-established way of storing electricity is in the form of chemical energy in batteries. As with the energy stored in fossil fuels in form of chemical bonds formed originally via photosynthesis, batteries also use the principle of chemical bond formation to store energy. Electrochemical storage is characterized as the ability to convert chemical binding energy directly to electricity. The process can be reversed for secondary (or rechargeable) batteries or accumulators in order to recharge the storage media. This approach has traditionally been used for small-scale applications. Only recently have large-scale applications of battery storage become of interest (Collinson 2001). Utility electricity storage requires a battery system that can be repeatedly charged and discharged, like the lead-acid battery used in cars or previously in portable computers. However, there the use of secondary batteries does involve some technical problems. Since their cells will slowly self-discharge, batteries are mostly suitable for electricity storage only for limited periods of time. They also age, which results in a decreasing storage capacity and ability to be recharged.

Because batteries can release their power virtually instantaneously, they can significantly improve the stability of an electricity network. For instance, after the Second World War, a large-scale battery storage plant with a capacity of 9.3 MWh and an output of 8.6 MW was constructed in Berlin to operate the city's island electrical system. Another system with an output of 10 MW and a four-hour grid capacity was constructed in California during the 1980s. It consisted of 8200 small lead-acid cells. There are many more battery energy storage systems in operation today. Smaller-scale storage options probably become more important in the future due to increasing capacity of intermittent renewable energy sources such as wind and solar. Costs and performance of new smaller-scale storage systems must be competitive to hydro-storage or systems using metal hydrides for hydrogen storage (compare Table 1).

a. Energy Storage in Batteries

Batteries use the energy involved in overall chemical reactions. Under general spontaneous exothermal reaction conditions, these only deliver heat. Because of the compartmentalization and controlled conditions inside a battery cell, the overall chemical reaction, or so-called cell reaction, is split into partial electrochemical reactions in two compartments connected through ionically conducting bridges in an electrolyte, and electronically conducting bridges in an external circuit. The battery cell can now release an electric current, i.e. exchange of electrons between the compartments, instead of heat only. The partial chemical reactions taking place in the different compartments are called reduction and oxidation reactions, either taking up electrons (positive electrode) or releasing them (negative electrode), respectively.

The performance of a battery is characterized by thermodynamic and kinetic parameters that depend on the materials and media used, and on the battery design. Thermodynamically, large chemical binding energy differences between the reaction partners, represented by a difference in reaction Gibbs energy, appears as a cell voltage. To achieve a high specific energy (Wh/kg), the electrochemical reaction partners or electrodes should be as light as possible. Conventional lead-(sulfuric) acid batteries store around 20 to 50 Wh/kg, which is low compared to petroleum fuel whose storage capacity corresponds to 10,000 Wh/kg of stored enthaply. Of course, conversion of this enthalpy to work takes place at less than the theoretical Carnot efficiency, and is usually in the 25-55% range with modern IC engine and gas turbine-combined cycle technologies. Significant improvements in overall delivered Wh/kg have been achieved with nickel/metal hydride and lithium-ion batteries as compared to older lead and nickel/cadmium batteries (Table 3). Besides the energy storage capacity of a cell, the speed and quality of recharge is often important for efficient and attractive applications of battery systems. Based on the solubility of reaction products or possible side reactions inside the cell, the recharging process can be inhibited or stopped completely after a few recharge cycles. In the following section, a short overview of different battery systems is given.

Table 3: Different battery systems used in applications today.

System	Electrolyte	Type	Storage capacity [Wh/kg] [a]	Application
Lead-acid	aqueous electrolyte (sulfuric acid), mostly immobilized	often sealed (valve-regulated), works at low temperatures, rechargeable	20-50	starter battery for cars, batteries for fork-lifts, electric vehicles, submarine, and ships (also unsealed non-maintenance-free)
Nickel-hydroxide cadmium	aqueous electrolyte, mostly immobilized	sealed (valve-regulated) rechargeable	20-55	battery system mostly for small equipment and some for propulsion, on-board electronics, and on-site applications
Nickel-hydroxide hydrogen gas	aqueous electrolyte, immobilized	Sealed, pressurized, rechargeable	50-60	battery system for many satellites
Nickel-hydroxide metal hydrides [c]	aqueous electrolyte immobilized	sealed (valve-regulated), rel. high load capacity, rechargeable	50-80	can replace nickel cadmium batteries
Sodium sulfur [d]	solid electrolyte (β-alumina) at temperatures of 300-400 °C	high temperature system, rechargeable	90-120	Electric vehicles, trams, buses
Sodium nickel-chloride [d]	solid electrolyte (β-alumina) at temperatures of 300-400 °C	high temperature system, rechargeable	90-100	Electric vehicles, trams, buses

Lithium-ion polymer, lithium cobalt oxide, lithium manganese oxide iron - or aluminum disulfide	organic electrolyte at room temperature	rel. high voltage (4V), rel. high load capacity, rechargeable	ca. 100	battery system for small applications, tests for some electric vehicles
Zinc bromine[b]	aqueous electrolyte	rechargeable	65-70	tests for some electric vehicles
Zinc air (oxygen from air) [b]	alkaline or neutral electrolyte	mechanically rechargeable, i.e. exchange of zinc electrode after a few cycles	ca. 170	tests for some electric vehicles

[a] when applied

[b] different battery system architecture, i.e. reactive substrates stored outside cell

[c] some nickel alkaline electrolyte batteries also work at low temperatures

[d] sodium-sulfur and sodium nickel chloride have been abandoned for traction applications

Source: Kiehne, H. A., Berndt, D., Fischer, W., Franke, H., König, W., Köthe, K. H., Preuss, P., Sassmannshausen, G., Stahl, U.-C., Wehrle, E., Will, G., and Willmes, H. (2000). *Batterien: Grundlagen und Theorie aktueller technischer Stand und Entwicklungstendenzen*, Expert Verlag, Renningen (with permission; adapted including additional applications).

In addition to the continuously improving efficiency of batteries, their other potential advantages are quietness, freedom from maintenance, their reduction of gaseous emissions and their independence of the nature of the primary energy carrier.

Electric batteries store direct current (DC) and can be easily integrated into domestic DC networks. An important parameter thereby is the charging (or load) factor that relates the necessary quantity of electricity in Ampere-hours (Ah) for the battery to become fully charged to the corresponding quantity released in the previous cycle. The time it takes to recharge a battery is strongly dependent on operating temperature.

Battery power is a flexible way to supply energy although it has limited applicability. For example, car starter, lighting and ignition (SLI) batteries provide electricity instantly at the turn of a key, but it is inconceivable to provide electricity from batteries to supply a city. The electric secondary battery is therefore well suited for certain applications involving instant, relatively low-voltage power, but it is unsuited for those on a large scale. Battery operation must be designed to be application-specific and must consider factors influencing cost, which often limit energy and power per unit weight and volume (energy and power density, specific energy and specific power) or durability (cycle lifetime, maintenance).

i. Battery systems for different applications

Battery powered motive systems for indoor use are a major area of application that take an increasing part in organized transport systems in automated industries. A good example is the fork-lift truck. The battery system provides flexible power for the traction vehicle, which is equipped with a recharging unit. The battery system design must include the energy supply system for recharge and is dependent on the kind of vehicle operation needed, i.e. capacitive operation with one full discharge/recharge cycle per mission, or cyclic operation with multiple synchronized missions, and combinations thereof. For internal transport tasks, electric traction equipment also provides a low noise, low emission, and clean mobility environment.

For road traffic**,** electric buses for public transport and electric cars are becoming more popular because for environmental reasons. A possible increase in fossil fuel costs may favor electrical motive power including the application of high energy density fuel cells for cars.

Intermittent storage of solar energy is another area of application. For example, for autonomous photovoltaic systems, the battery sub-system must be designed to cope with wide fluctuations of input and output currents. The average electricity consumption of powered units and the average availability of solar radiation need to be balanced using site and application specific battery systems.

Other immobile battery systems are used in the telecommunications business, often as back-up safety systems to compensate for loss of electricity supply from the grid. These systems must be designed to close the supply gap for several hours and in some cases high power outputs must be available immediately or within minutes. As back-up systems for power outages, the systems must be durable and reliable even if they are rarely put to use.

The specific property of providing high power in a relatively short time is also necessary for starter batteries, for instance for vehicle engines. These must supply a broad load profile with up to 20 A to 70 A during idling or slow drive and 300 A for up to 3 sec during the starting operation.

Mobile systems

Early in the 20th century vehicles using lead-acid batteries traction batteries out-numbered internal combustion (IC) powered vehicles. With the invention of the self-starter and development of a refueling infrastructure along the commercialization pathway of the car, the combustion engine using the higher energy densities of fossil fuel**s** rather than electricity showed a far greater range per charge of energy. A lead-acid battery of a given weight could only store electricity equivalent to 1% of its weight in gasoline, which has a heat content of 13,000 Wh/kg in contrast to 25 Wh/kg of an early lead-acid battery. We should note that in the last 100 years batteries have improved only by about a factor of two (Ristinen and Kraushaar 1999). Even taking into account the low energy conversion efficiency of gasoline to power, compared with the efficient end-use of electricity, the battery still severely limits electric vehicle range.

The problem with electric vehicles is clearly the storage of electric power. No battery can have the energy density of gasoline, and battery recharging is far slower than filling a tank. Battery lifetimes also require improvement, and much lighter and non-toxic battery materials must be found to replace heavy metals such as lead. An interesting concept now being tested is a hybrid vehicle with a small, efficient internal combustion engine to recharge its batteries and to drive the vehicle after the electric motor has accelerated it. Regenerative braking also helps to charge the batteries; and because of the reserve electric motor, the IC engine can be quickly restarted after every stop and need not idle, thereby resulting in high fuel efficiency (Dresselhaus and Thomas 2001).

Substitution of the decentralized, fossil-fueled car, truck and bus fleet of today with fuel cell driven vehicles is an important future task which is already in progress. For instance, the Ford Motor company expects a fuel-cell-powered version of its Ford Focus sedan may become commercially available for use in company fleets by 2004. This car will combines high- pressure hydrogen gas storage with a fuel cell to achieve a peak power output of 90 horsepower and a peak torque of 140 foot-

pounds. The vehicle has a top speed of greater than 80 miles per hour and a range of 100 miles. In contrast, research and development of electrical vehicles with lead acid, nickel-cadmium or nickel-metal hydride battery, or molten salt sodium β-alumina batteries have not achieved the required reduction in weight and volume to be competitive with the conventional fossil-fueled IC engine. It is expected that mobile fuel cells for transportation will gain large market shares in the next few decades. Technically, stationary fuel cells can also be used for public mobility as centralized electrical energy supply for trams and trolleys, underground (subway), light and conventional rail, and high-speed trains, if high power storage such as SEMS and ultra-capacitors become available. From an environmental perspective, complete electrification of the vehicle fleet of gasoline-fueled, light-duty, internal combustion engines including the complete fuel cycle in each case, and based on the 1997 Alabama (USA) generation mix, would provide a 44% decrease in NOx emissions, an 18% decrease in CO_2 emissions, but a 14% increase in SO_2 (Lindly and Haskew 2002). However, the linear extrapolation based estimate will drastically alter when installing new modern plants and technology to satisfy electricity and mobility demand.

Immobile systems
For large on-site immobile battery systems mostly lead-acid or nickel based batteries are used today in power plants and solar installations, signal transmission (Telecom, radio) and uninterrupted power supply (UPS) systems, switchgear installations, annunciator and traffic lights, safety or emergency lighting, and air conditioning installations[2]. Because of the characteristics of their application, high reliability is required. For telecom equipment, batteries need long operating times to balance electricity supply outages of several hours. For UPS systems, batteries must be able to instantaneously release very high currents over short times (minutes) until the back-up system responds. Less than a 0.25% failure rate has been observed with lead-acid and nickel-cadmium batteries in such systems. Safety and durability are most important criteria. In addition, sealed valve-regulated lead-acid batteries are often chosen also because of their low maintenance requirements.

High energy density batteries
Electrochemical power sources can be classified into accumulators or secondary cells having cells containing all corresponding reactive components, and fuel cells where reactants (e.g. H_2 and O_2) are fed to the cells when power is needed. Their battery performance is judged according to the power gain per weight and volume of the battery system, the life cycle, durability and the cost per weight. Although many different high energy density battery systems are being developed, all of these criteria have yet to be simultaneously fulfilled. The most important high energy density battery systems are summarized in Table 4.

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[2] Darnell Group, Inc., Worldwide Battery Pack Market Forecasts,
  http://www.darnell.com/services/o2-bckup_strg.stm

Table 4: Properties of some secondary batteries and fuel cells.

Class	System	Type	Operating Temperature °C	Electrolyte	Energy density[1] Wh/kg	Power density[2] W/kg	Lifetime charging cycles/ years charged
Accumulators	Lead-lead oxide system	Pb/PbO$_2$	<45	H$_2$SO$_4$	161/35	80/160	750/>3
	Lithium-metal sulfide (oxide) system[3]	Li/TiS$_2$	Ambient	Polymer	473/100	35/400	300/1
	Lithium-iron sulfide system	Li/FeS$_2$	400	Salt melt	650/180	30/400	1000/0.9
	Zinc-bromine system	Zn/Br$_2$	60	ZnBr$_2$+H$_2$O	430/55	70/80	400/2
	Sodium-sulfur system	Na/S	320	Ceramics	758110	95/150	4000/4
	Sodium-nickel chloride system	Na/NiCl$_2$	300-400	Ceramics	65082	60/140	2000/-
				Fuel	max. power W/cm^2	max. operation time in hours	
Fuel cells	Low temperature fuel cells	H$_2$/Air	<100	Polymer	H$_2$ or MeOH	1500	1200 (1kW module)
	Mid temperature fuel cells	H$_2$/Air	>100 - 200	H3PO4	Natural gas	150	16000 (several MW)
	High temperature fuel cells	H$_2$/Air	600	Carbonate melt	Natural gas, gasification	150	5000 (3kW module)
	High temperature fuel cells	H$_2$/CO/Air	1000	Ceramics	Natural gas, gasification	300	40000 (cell)

[1] theoretical / experimental: The theoretical value accounts only for the weights of the reaction substrates. The experimental value accounts for a 5h discharging time, except for the Sodium-sulphur system, which has 1h.
[2] continuous operation/ pulse operation (30sec)
[3] other combinations include /MoS2, /NbSe, /V2O5, /CO2
Source: Kiehne, H. A., Berndt, D., Fischer, W., Franke, H., König, W., Köthe, K. H., Preuss, P., Sassmannshausen, G., Stahl, U.-C., Wehrle, E., Will, G., and Willmes, H. (2000). *Batterien: Grundlagen und Theorie aktueller technischer Stand und Entwicklungstendenzen*, Expert Verlag, Renningen (with permission)

The reactive materials are stored inside the conventional secondary cells, whereas the fuel cells store them outside the cell stack. The systems are also distinguished according to their operating temperature and electrolyte. Important parameters are the energy and power density, and lifetime. High temperature secondary batteries and fuel cells are somewhat in competition to gain future shares in the electric vehicle markets. In recent years the fuel cell has received a great deal of attention since it offers good performances in lower temperature operation and it allows a much improved electric vehicle range.

Regenerative fuel cells can be used to store electricity in a chemical form, and convert the stored energy back into electricity when needed. A regenerative fuel cell plant could be designed to store more than 100 megawatt-hours (MWh) of energy and provide power for hours to several thousand homes. Such plants[3] would mainly

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[3] http://www.tva.gov/news/releases/1001storageplant .htm

store energy during periods of low demand and produce energy during peak periods. The development of regenerative fuel cells is still confronted with many obstacles, particularly regarding pole reversal and recharging cycles. However, new developments have been achieved with one type of regenerative fuel cell, the redox-flow battery. This cell stores electricity in liquid (dissolved) form and in such a way that the maximum storage capacity can easily be increased by increasing the storage capacity of the electrolyte. The energy density is 20 to 30 Wh per liter, which is about 30% of a normal lead acid battery. Therefore redox-flow batteries are relatively large and heavy, which makes them only suitable for stationary applications. A large-scale application with a capacity of 15MW/120 MWh has been built based on the Regenesys™ regenerative fuel cell[4] employing the bromide/tribromide and the polysulfide/sulfide couples in aqueous solution. Technical and economic data, according to National Power PLC are given in Table 5.

Table 5: Characteristics[1] of Regenesys™

Power:	15 MW maximum
Storage capacity:	120 MWh
Footprint:	<5000 m^2
Storage tanks:	2 tanks of 1800 m^3 each
Total installed costs:	US$ 22 million
Liftetime:	15 years
O&M-costs:	relatively small (unmanned facility)
Storage time:	10 hours
Capital costs:	US$185/kWh ! US$50/kWh (mature technology)
Overall efficiency[2]	70%

[1] Renewable Energy Wold/January2000
[2] http://www.electrosynthesis.com/news/w8content.html

Batteries for photovoltaic energy supply
Energy storage has always been closely associated with solar installations, including both solar heating and photovoltaic (PV) applications. Although today photovoltaics can be grid-adapted, the problem of the intermittent nature of solar energy can be solved either through energy storage or by system back-up, such as the use of natural gas burners at night or on cloudy days (Owen 2001; Witt et al. 2001). For rooftop solar power systems, possible applications include battery storage systems with the option to expand the power output from a standard 2.4-kilowatt to 3.2 kilowatts. Table 6 lists many more storage applications for PV supply technologies.
In order to find the optimal system dimensions for the specific storage application, the average electricity consumption and the diurnal consumption profile should be known. Other very important parameters are those of the PV cells themselves, which for instance must be adapted to the seasonal variation of solar radiation. Since seasonal storage is not considered for small systems, additional power installations, for instance hybrid systems, are required to cope with seasonal differences.

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[4] Large-scale storage solution? Regenesys[TM] regenerative fuel cell. Renewable Energy World, January 2000, pp. 85-91.

Table 6: System power range for PV storage applications.

Power range	Typical application	Examples
μW	Integrated transistors or chips with minimal energy consumption	Solar watches and calculators
mW	Equipment and installation with low energy demand and only periodic use	Portable receivers / transmitter, automatic devices like ticket or vending machines, fire or security alarm systems
W	Installations for communication and measurement, small consumer households or businesses	Devices on buoys or for TV, radio and meteorological stations, electricity supply on boats or in holyday houses, electricity supply for heat pumps.
KW	Stand-alone grids with electric equipment and installations	Remote estates, military

Source: Kiehne, H. A., Berndt, D., Fischer, W., Franke, H., König, W., Köthe, K. H., Preuss, P., Sassmannshausen, G., Stahl, U.-C., Wehrle, E., Will, G., and Willmes, H. (2000). *Batterien: Grundlagen und Theorie aktueller technischer Stand und Entwicklungstendenzen*, Expert Verlag, Renningen (with permission)

ii. Batteries and the Environment

The increasing use of secondary batteries, especially lead-acid or nickel-cadmium batteries, means hundreds of tonnes of toxic heavy metals are discharged yearly into the environment. Potential environmental impacts from their improper disposal, has been recognized as a problem not only in the developed countries but also in developing nations. In Europe the 1992 Government Action Plan for Waste and Recycling and the 1992 Waste Management Plan for Municipalities consolidated the framework of the Environmental Protection Act 1994. In the U.S., it was the 1996 Mercury-Containing and Rechargeable Battery Management Act, the "Battery Act", that promoted the collection and recycling or proper disposal of used nickel-cadmium and lead-acid batteries, clear labeling of batteries, and education of the public about recycling and disposal. The U.S. Battery Act also limits the mercury content in some consumer batteries. Another goal is to phase out the use of mercury in batteries and provide for the efficient and cost-effective collection and recycling or proper disposal of used nickel cadmium batteries, small sealed lead-acid batteries, and certain other batteries.

However, the recycling systems seem to fail: As shown for Germany, the contents of only one third of the cadmium-containing batteries find their way back to the retail shops, although throwing them into household waste has been widely banned. It is now suggested to phase out the use of nickel-cadmium batteries from a wide range of applications, e.g. household appliances, in order to stop the highly toxic cadmium input to the environment. For consumer use, nickel-cadmium batteries are now restricted to demanding markets, e.g. power tools requiring very rapid discharge. Another proposed measure is to enforce dramatically lower amounts of cadmium in batteries stepwise, which will ultimately require a change to alternative systems. Alternative secondary battery systems are lithium and nickel-metal hydride batteries. Still, all new or alternative systems must be examined using material flows from cradle to grave. For electric vehicles, for example, lead is a key material of concern. Where possible, nickel metal hydride is now used, e.g. in hybrid vehicles. But lead-acid batteries are mostly being considered as a viable and cheap energy storage choices for ordinary electric vehicles. Secondary lead smelters are the facilities

where used batteries are recycled into usable lead. Lead-smelters seem still to be the key source of lead released to the environment (Maxwell and Kastenberg 1999). The development of fuel cells for cars, trucks and buses will reduce the environmental impact of the mobility today, even if natural gas feeds the fuel cells in transition. However, only if hydrogen supply and storage technology are developed and the hydrogen is generated from regenerative sources will the balance tilt significantly towards "green mobility".

b. Ultra- or Supercapacitors

Capacitors are energy storage devices, which use charge as a storage mechanism. A conventional capacitor with charge +Q on one plate, -Q on the other, and voltage V between them, has a stored energy equal to 1/2 QV. Almost all capacitors use a dielectric material between the plates, which optimizes charge distributions along the atoms of the material through re-arrangement. Dielectric material with a high polarizability allows a capacitor to store a large charge having applied much less voltage. Dielectric capacitors can provide power densities many times more than 1 kW/kg and have very long cycle lifetimes, whereas batteries provide less than 0.2 kW/kg and fewer cycles (generally 100-1,000). In contrast, dielectric capacitors have energy densities less than 1 Wh/kg, whereas batteries can provide over 100 Wh/kg. The applicability of dielectric capacitors is therefore clearly limited to a few specific tasks requiring high power at high voltages over very short time periods, e.g. for lasers. Super-conducting inductive systems have similar limitations (see Section 3a).

Having storage systems available that can provide several kW/kg power output combined with several Wh/kg specific energy, at the same time permitting thousands of recharge cycles are important technological goals for the future. Supercapacitors (Scaps) are devices with the potential to achieve the necessary performance and have therefore received considerable attention in research and demonstration during the last decade. Some Scap devices are commercially available today.

Scaps are electrochemical (EC) capacitors, which are often made with carbon or another high surface area material as the conductor and with an aqueous or non-aqueous electrolyte. EC capacitors can provide both power and energy, leading to performances with more than 1 kW/kg specific power, and over 5 Wh/kg specific energy, with high cyclability (many thousands of cycles). In addition, when EC capacitors are coupled with batteries, they can reduce the peak power requirement, prolong the battery lifetime and reduce the energy requirement (or the size) of the battery. The batteries provide the energy, and the EC capacitors provide the instantaneous power needed. Applications include acceleration power for electric vehicles, electrical regenerative braking storage for electric drive systems, power assist to hybrid vehicles, starting power for fuel cells, pulse power for mobile telecommunication and other electronic devices that require high power to operate.

Scaps, also known as ultra-capacitors or electrochemical double-layer capacitors, are new passive components, which are used in power electronic applications. They have a huge capacitance, typically 1000 F (Farad = 1.0 Coulomb or Ampere-Second per Volt), which is about 500,000 times larger than conventional capacitors (typically 2000 μF). They show performance, which lies between that of batteries and conventional capacitors (see Subsection i). The capacitance is due to the accumulation of electronic and ionic charges at the interface between the electrodes

and the electrolyte. Scaps are high-density energy storage cells that deliver bursts of high power on demand in applications such as automotive electrical systems and power trains, wireless communications, and consumer and industrial electronic devices. Compared to batteries, Scaps cannot be used alone, and must be associated with a power supply system. They can be used as energy buffer bank to minimize the constraints on power supply. Depending on the configuration, a sequential distribution of a double storage Scap system can be used both as main energy source and as energy buffer bank, or applied for instance as load equalizer for elevators. Scaps have a wide scale of potential applications like memory backup-systems, or in hybrid systems combined with fuel cells or battery systems, e.g. hybrid vehicles. Scaps reduce the duty cycle of fuel cells or battery systems resulting in a considerable increase of the specific power production of these systems. The storage capacity of Scaps is limited, making them less suitable for large-scale electricity storage.

High-durability large-cell Scaps are designed specifically to meet the energy storage requirements of the transportation and industrial markets. Low-cost Scaps are expected to become the standard option for energy storage systems of consumer electronics, industrial and transportation markets with an 80 percent cut of material costs[5]. Large market opportunities are therefore expected to generate significant ramp-up in volume in the next few years. The unit prices of large cells are expected to fall from presently $150 to less than $30, based on projected manufacturing cost reductions that could be realized with new designs.

Scap's low cost, 'life of the vehicle' durability, their ability to discharge and recharge rapidly, operate reliably in extreme temperature conditions, absorb energy disruptions efficiently and their environmentally cleanliness make them an ideal choice for many applications. For instance, Scaps can be used as storage components in electrical systems of auto, truck and buses enhancing 12- and 42-volt electrical systems for safety features, conversion of mechanical functions, such as steering, braking and air conditioning and more efficient all-electric systems.

Hybrid electric bus, truck and auto power trains that reduce fuel consumption and emissions by using electric power to assist acceleration and recapturing and reusing energy from braking. Scaps can also be used in stationary industrial power applications, as low-maintenance, solid state alternatives to batteries for short-term bridging in uninterruptible power supply (UPS) systems, or for peak load buffering to increase efficiency and reduce the size and cost of stationary energy systems such as fuel cells.

Scaps are also well suited to be incorporated into photovoltaic powered systems to enhance the system's capability. Such photovoltaic/supercapacitor combined power sources can operate under adverse conditions, and/or satisfy or meet regulations otherwise more difficult to achieve with conventional battery driven systems.

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[5] Maxwell Technologies 2002;
  http://www.maxwell.com/ultracapacitors/news/inthenews.html

3. Electro-magnetic systems

a. Superconductivity

Superconductivity has the potential to dramatically change the generation and use of electricity. It offers the ideal way of storing electric power directly using super-cooled inductive coils. In principle, much higher storage capacities than in conventional capacitive or inductive systems are achievable having short time releases at various voltages; the costs however, are enormous.

Superconductors are being considered for superconducting magnetic energy storage (SMES), where electric energy is stored by circulating a current in a superconducting coil. Because there are no resistive losses, the current persists indefinitely. At present, niobium–titanium alloys are used for storage at liquid helium temperatures, 2-4 K. To use super-conducting materials with higher critical temperatures for these energy-related applications, e.g. 60-70K, the temperature of the much more practical and cheaper liquid nitrogen, will require additional research and development (Larbalestier 2001). The efficiency of charging and discharging is very high because no energy conversion is involved, and for the same reason SMES can respond rapidly, with a response that is limited by the time required for conversion between DC and AC power. Rapid respond within a few seconds make SMES attractive for system stabilization or primary regulation of the electricity grid. Probably the first applications of this technology are load leveling, and frequency and voltage control. At the moment only SMES with a relative small storage capacities for power grid stabilization or industrial plants are commercial available (American Superconductor[6]). This SMES technology combines conventional low-temperature material with high temperature super-conducting (HTS) materials. In the development of new equipment for electricity supply systems, electrical energy SMES target to provide storage capacities of some 100 kWh, while superconductivity permits a compact system design. Larger SMES systems are not yet available.

Large-scale applications of superconductors for energy storage will depend on achieving high critical current densities (Jct) to be cost-competitive with other technologies. The unit costs of power stored in a super-conducting ring decreases with increasing plant size. Research is aimed at increasing the fraction of the cross-sectional area of the super-conducting wire actually carrying the high current density. Both physics and materials science issues are being tackled. For all of these applications, high powers and enormous magnetic fields will be involved, so careful consideration must be given to the consequences of an accidental loss of coolant; a huge amount of energy would be released at the instant the superconductor became a normal conductor; 10 MWh of stored energy is equivalent to 1.18 tonnes of TNT. A super-conducting ring for a 5,000 MW plant would be roughly 1,600 meters in diameter. Although the superconductivity business is expected to be large by 2010, it is too early to judge as to whether super-conducting power storage, generation and power transmission will soon become competitive. Technological development of electrical energy storage via superconductivity will require time and large investments. SMES technology with 90% efficiency for storage of excess night-time electrical energy should be economically comparable

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[6] http://www.amsuper.com

with water-storage technology with efficiencies of 65-70%. To show the magnitude of the technical problems involved, 2 million tons of structural material will be required to confine 10 million kWh of stored energy, which is similar to that for water storage systems. A construction period of 4 years for a superconducting magnet, and 7 years including digging the rock base has been estimated (Masuda 1988).

As mentioned earlier, ceramic superconducting materials could be very useful in flywheel systems running on frictionless magnetic bearings made from superconducting materials.

C. Thermal Storage Systems

Since ancient times the underground has been used as constant temperate zone for food storage. One of the oldest energy storage activities was gathering ice from frozen lakes and rivers. The ice stored in well-insulated rooms was used to preserve food, cool drinks, and condition indoor air for which mechanical refrigeration is used today. Since the 20's century the underground is used for active thermal storage for cooling or heating of buildings or for industrial processing.

The energy content E of a thermal energy storage volume V is proportional to the temperature before (T_1) and after (T_2) recharge, i.e. $E = C(T_2-T_1)V$. C is the specific heat per unit volume; a storage media or material specific coefficient. Water has a high specific heat of 1 kcal/kg·°C as compared to steel with 0.1 kcal/ kg·°C. The transferred energy involved in temperature changes of materials is called sensible heat, while the energy involved in changing the phase of a material is called latent heat. Depending on restrictions of volume or pressure changes in gaseous or liquid storage media, the specific heat of constant volume C_v, or of constant pressure C_p are important parameters to design efficient thermal energy storage systems.

Heat and cold storage systems are important for short-term and long-term (seasonal) storage. The purpose of short-term storage generally is to store power that of long-term storage is to store energy. One of the benefits of short-term storage is to shift electric resistance heating to off-peak hours. Environmental benefits include the possibility of using renewable energy sources to increase the demand coverage, e.g. use of solar power to reduce conventional heat sources. The benefit of long-term storage is that by balancing seasonal discrepancies in supply, for example from waste heat, CHP units or solar power, and in demand, e.g. additional heating demand in winter or cooling demand in summer, energy consumption can be significantly reduced.

For present short-term storage, the following systems exist:
- water, standard medium for heat storage,
- ice (phase change at 0°C, latent heat provides large energy density)
- phase change materials (salt hydrates), allow phase change at other temperatures than 0°C, currently in market introduction phase,
- sorption systems (e.g. H_2O/SiO_2, silica gel), in experimental stage, due to high energy density also suitable for long term storage.

Other relevant parameters for thermal systems are energy losses as a percentage of the retrieved thermal energy, which depends on energy density, reflux temperatures, insulation quality, surface to volume ratio, and the duration of storage. The energy density (kWh/m^3) depends on the temperature level stored in a media of specific heat capacity. The cost of thermal systems depends on volume and energy stored (Table 7).

Table 7: Overview current situation for short-term storage

	Energy density [kWh/m^3]	Energy losses (estimate) [%]	Cost (<10 m^3) [US$/m^3]	Cost (>100 m^3) [US$/m^3]
Water	50-60*	20%	2000	700
PCM	50-120	12%	2700	1300
Adsorption	200-250	5%	6800	4500

Source: Collinson, A. (2001). "Daces 2050: Database Clean Energy Supply 2050." Netherlands Ministry of Housing, Spatial Planning and the Environment; UCE, Utrecht Centre for Energy research; STS, Dept. for Science, Technology and Society, Utrecht University; ECN, Netherlands Energy Research Foundation; Ecofys, Energy and Environment; RIVM, National Institute of Public Health and the Environment (adapted)

Water as thermal storage media has a low energy density and consequently needs larger volumes, with correspondingly large heat losses. Especially for long-term storage the surface to volume ratios ratio should be as small as possible. The recovery efficiency of heat from thermal storage depends on the reflux temperature of the heat extraction system. Improvements are possible in combination with heat pumps, although more costly. Also, more effective storage media should be developed.

Technological advances of phase change materials (PCM) can increase the thermal mass per unit floor area of buildings and more specifically can improve the efficiency of thermal systems. Large cost reductions and improvements of additives are necessary to achieve within the next decades. Adsorption systems have a large potential for seasonal storage applications of solar thermal energy at the level of single homes. The heat coverage with solar thermal energy could technically reach 90-100%. These systems seem most suited for homes where less cooling is required.

Another technological straight include the development of thermochemical systems based on the reaction energies of chemical couples. Thermochemical couples like sulfur oxides and oxygen, or carbon oxides and hydrogen are interesting because chemical compounds having high energy densities are possible to be transported over long distances through pipes without heat loss. Heat will than be released at the spot of demand using for instance combined heat and power (CHP) systems or fuel cells.

Long-term storage is often combined with solar thermal systems. Soil-heat exchangers integrated in pile foundation, soil or groundwater systems (aquifers) are used. The energy used for circulating the storage media water through the system is determined by the permeability of the underground in use and its depth. The corresponding net thermal energy retrieved, the size, and the temperature levels of the system are the most important system characteristics. The costs are strongly determined by the required pumping capacity (m^3/h) and power capacity (kW), and less by the size of the system (Table 8).

Table 8: Overview the current situation of seasonal storage

	Pumping capacity [m³/h]	Power capacity [kW]	Pumping energy [%] of useful energy	Cost [US$/m³h⁻¹]
Soil heat exchangers	0.5-50	5-450	5-8	1800-4100
Groundwater system	10-500	100-4500	5-8	1600-2700

Source: Collinson, A. (2001). "Daces 2050: Database Clean Energy Supply 2050." Netherlands Ministry of Housing, Spatial Planning and the Environment; UCE, Utrecht Centre for Energy research; STS, Dept. for Science, Technology and Society, Utrecht University; ECN, Netherlands Energy Research Foundation; Ecofys, Energy and Environment; RIVM, National Institute of Public Health and the Environment (adapted)

Technically, solar heat can cover 90-100% of required space heating in homes today. However cost are above US$ 10,000 per home (5000m² floor area). For cooling demand, underground soil or groundwater systems are very productive, especially if improved building construction, (automated) shading systems, highly efficient lighting systems and electric appliances reduce cooling demand to a minimum. A combination with energy conservation strategies allows for these cooling systems to cover the entire cooling load in most office buildings. In winter the same system can be used to preheat the cold air drawn in for fresh air supply in office buildings, reducing heating demand by about 30%. Seasonal underground storage systems can even provide coverage of up to 70% space cooling in industrial buildings having cooling capacities of 40-70 W/m². The costs are around US$ 300 per kW. Underground storage systems cost around US$ 100'000 per building.

1. Water for Thermal Energy Storage

a. Thermal storage tanks

Centralized water thermal storage is by far the most common form of thermal energy storage today, e.g. hot water storage used with cogeneration plants. Usually bigger underground hot water storage tanks are buried underneath large infrastructure components like athletic or football fields, parking lots and garages having capacities of a million gallons or more. These large capacities are conventionally used with welded steel tanks, reinforced concrete or wire-wound concrete tank systems. According to storage needs, heat storage capacities range from 60 to 80 kWh/m³.
Low heat conducting tanks (<0.3 W/m²·K) have been recently developed in Germany using fiberglass composite materials. These innovative tanks are applicable for buffer and short-term storage in the range of hours and days having volumes between 5-10 m³, for storage in the range of weeks with volumes between 50-100 m³, and for long-term, seasonal storage with volumes between 500-6000 m³, delivering thousands of ton-hours hot water storage. The cost of large tanks (6000m³) are presently around 100 $/m³. Such tanks can also be used to store cold water.
Other thermal storage systems used for cold water storage are based on stratified storage underground tank systems combined with linear diffuser system in order to reduce inflow turbulences. The different temperatures contained in a thermally stratified storage tank hold the density variation of warm and cold water on top and the bottom, respectively. Thermally stratified storage tanks are an effective

technique that is widely used in energy conservation and load management applications. It is commonly applied in combination with solar energy or waste heat reuse systems. The thermal stratification improves the efficiency of storage tanks as heat at intermediate temperatures can be used to heat colder layers below and withdrawn without disturbing stratification too much. System parameters include various inlet and outlet locations, velocities, temperatures and heat loss. Heat conduction at the tank walls and heat loss to the ambient through the cover strongly influences the stability of thermal stratification.

Long-term heat storage in combination with waste heat distribution, solar or CHP systems are also constructed using man-made water permeable gravel pits insulated and covered with heat damming materials like polypropylene foil, vacuum insulation foil, and glass granulates. Storage temperatures are around 90°C. Heat storage capacities are between 30-50 kWh/m^3. Volumes of 1000-8000 m^3 have been successfully installed at several places in Germany. Cost for large systems (around 10,000 m^3) are around 75-150 $/m^3. Future cost reductions should accomplish less than 50 $/m^3.

Short-term or buffer heat storage systems are ubiquitous for in-house generation of hot water in heater or boilers. The size of decentralized heat storage systems depend on the water boiler output power needed to satisfy the buildings hot water and heating demand. A minimum of 25 liters storage volume per kW boiler output is needed; for more comfortable operation 70 L/kW is recommended. Decentralized thermal storage heater/boiler systems mostly use electrical night currents for electrical resistances heating. The heat is stored for later use. An important aspect of the short-term storage concept is to maintain thermal stratification. The performance of storage-type domestic electrical water-heaters is greatly improved and energy conservation optimized. Designs are dependent on draw-off rates (usually 5 to 10 L/min) with the placement of heating elements and residence time being important design parameters. Optimized ratios of tank size and draw-off rates together with better thermal stratification inside the heater storage tank results in higher discharging efficiencies.

b. Large underground thermal energy storage systems

Building, industrial and agricultural sectors require larger thermal storage dimensions. There are three forms of underground thermal storage systems (UTES) normally used:

- Thermal underground storage tubes (e.g. soil heat exchanger) which require large storage volumes to improve storage efficiency achieving 15-30 kWh/m^3
- Aquifer storage system with reduced storage volume but site specific requirements achieving 30-40 kWh/m^3
- Man-made cavern storage system with confined storage volumes 40-60 kWh/m^3

Early adoption of energy storage in standard project designs is essential to improve their energy efficiency. In non-sealed UTES systems, heat is normally stored at around 15-40°C, while cold storage areas are between 5-25°C. Depending on the size of the area used, heat/cold storage capacities of up to 5-6 GWh per year are achievable. Relative new concepts of high-temperature underground thermal energy

storage (HT UTES) at around 70-90°C are attractive to achieve more economically efficient and environmentally benign energy systems with reliable long-term operation. Other types of UTES-systems are confined to aquifer storage (ATES) and duct/borehole storage (DTES) that can store waste heat from municipal facilities in summer, and providing domestic hot water and space heating in winter. Large-scale thermal storage systems must be technically, economically, and environmentally evaluated. Chemical aspects of thermal energy storage in the aquifer must be investigated in order to solve clogging and environmental heat exchange problems. For example, at high temperature ATES consisting of vertical wells with horizontal drains, major problems can occur at the heat exchange interface where major amounts of calcite can be formed. Additionally, developing and testing site-specific ground-water treatment methods regarding the chemical, microbiological and environmental effects help to meet necessary environmental standards. Adequate scaling of ATES improves reliability and avoids or reduces potential ecological impacts. Large-scale, innovative and cost-effective seasonal heat/cold storage applications are attractive for a variety of building types and industrial applications. Early adoption of cold storage as a standard design option including improvement of effective storage control and operating strategies to combine hot and cold storage should be encouraged in order to increase energy efficiency and cost effectiveness (IEA 1997). Recently, a heat/cold combined ATES has been installed in Berlin for the new governmental building complex using two separated aquifers at different levels; one at about 60 m for cold storage and the other at about 300 m for heat storage. The storage system is coupled with a heat pump, and, in case of extra load necessary in winter, with a CHP unit running on biofuels. Reaching its full operation, this ATES system should ultimately provide 16 GWh heat and about 3 GWh cooling capacities.

Man-made cavern storage systems are placed in leak-tight granite, gneiss, or hard sediment rock confining storage volumes. Having low heat conducting properties, caverns can store heat at temperatures around 90°C. A recent example is the cavern storage system of Lyckebo in Schweden. It has a storage volume of about 100,000 m^3, and a heat storage capacity of 5.5 GWh.

2. Latent Heat / Phase Change Systems

Although being inexpensive, readily available, and having excellent heat transfer characteristics, water as a storage media needs large volumes to achieve adequate heat storage capacities. Other thermal energy storage systems are used where space is limiting. Often phase change systems are applied which make use of latent heat. Latent heat is the energy required to change the state of a unit mass of material from solid to liquid or liquid to gas without a change in temperature.

Latent heat storage installations using PCMs or chemical reactions for thermal energy storage are alternative concepts for specific applications in building systems, or specific processes in the agricultural and industrial sector. Though these advanced thermal energy storage techniques have to overcome technical and market barriers. Long- (seasonal) or short-term phase change and chemical reaction thermal energy storage are attractive for energy savings and the reduction of peak demand. The oldest phase change material (PCM) in thermal storage is ice. Today, ice is often used in glycol static ice system with phase change at 0°C and an energy density of about 90 Wh/kg for its cooling service. Glycol static ice systems cost

more than cold water systems, but they require less space. Heat storage at different temperatures can also be designed using other PCMs (Table 9). The overall temperature required to melt the PCM must be considerably less than what the output of a heating system provides. Compounds with the lower melting points are therefore more desirable.

Table 9: Transition temperature and latent heat energy of some types of the most common groups of PCMs.

Group	PCM type	Transition temperature (°C)	Latent heat (Wh/kg)	Thermal conductivity, liquid / solid (W/mK)
Inorganic salt hydrates	Calcium chloride	27-30	47-53	0.54^a / 1.09^b
	Sodium sulfate (Glauber's salt)	32	70	-
	Zinc nitrate	36	41	0.46^c / -
	Magnesium nitrate	89	45	0.49d / 0.61e
Organics	Polyglycol E400	8	28	0.19^f / -
	Polyglycol E600	22	35	0.19^f / -
	Octadecane	28	68	-
	Ecosane	37	69	-
	Paraffin 116 (paraffin wax)	48	58	-
	Paraffin 6403 (paraffin wax)	62-64	48-53	0.17^g / 0.35^h
Fatty acids	Palmatic acid	63	52	0.16^i / -
	Capric acid	32	42	0.15^j / -
Organic/inorganic mixes (Eutectics)	Mystiric acid (mainly inorg.)	54	52	-
Aromatics	Naphtalene	80		0.13^k / 0.34^l

[a] 38.7 °C, [b] 23 °C, [c] 39.9 °C, [d] 95 °C, [e] 37 °C, [f] 38.6 °C, [g] 63.5 °C, [h] 33.6 °C, [i] 68.4 °C, [j] 38.5 °C, [k] 83.8 °C, [l] 49.9 °C

The transition temperature (melting point) and density of the solid phase are related to the specific heat and thermal conductivity of the solid and liquid phases and must be compatible with the site conditions of the application. In general, organic PCMs are more expensive than inorganic salts but can be custom made to provide transition temperatures specific for a given application. Compared with inorganic salts, they are non-toxic, non-corrosive, non-hygroscopic, more stable during repeated phase change cycles, compatible with most building materials, have generally higher latent heat per unit weight, melt without remaining solid phase sediments, and most importantly show negligible supercooling tendencies. Some disadvantage of organic PCMs may be its potential flammability. Nonetheless, organic PMCs are used in buildings today, for instance to absorb solar heat for air heating. Eutectic PCM behave as salt hydrates but can be custom made in order to meet specific melting points. However, the costs are considerably higher than organic or inorganic PCMs.

PCM modules consist mostly of series of PCM filled plastic pipes embedded in insulation material. The heating pipe system passes through the modules in order to exchange heat. In combination with thermal stratification tanks, flat PCM modules with different melting temperatures can enhance efficiency, because of stopping heat

conduction at surfaces and therefore improving the stability of the stratification. This method can also be used for larger centralized thermal storage tanks.

3. Other thermal storage systems

A very different thermal storage system is based on thermophysico-chemical properties of different chemical compounds. For example, cooling is achieved in chemical heating/cooling pipe systems by the endothermic heat of mixing of solid- or liquid- liquid mixable materials. Evaluation of the most suitable mixing-pairs in terms of cold/heat capacity must be carried out for each specific application. In solid-liquid pairs, urea/water and ammonium nitrate/water are found to generate endothermic heat of 8.2 kW/kg as soon as the materials are mixed. Similarly, iso-butanol/acetonitrile and 1-butanol/acetonitrile are found to produce 0.8 kW/kg. For regeneration, waste heat of 80°C can be used to redistill the mixtures.
Recently, very innovative latent heat storage systems have been developed using molecular adsorption and desorption on chemical surfaces, which were integrated in ventilation systems. Having very large surface areas, zeolites are ideal materials that adsorb water vapor effectively releasing a lot of adsoption heat. This discharging process can heat inlet air from 25°C to 100°C streaming at 6000 m^3/h through 7 t of zeolites and providing a heating power of 95 kW for 14 h per day. During low heat demand, the charging process takes in air streams of 130°C, in order to desorb the water molecules from the zeolite surfaces, releasing a humidified air stream at 40 °C. The storage capacity is around 150 kWh/m^3 of zeolite material. The system has been successfully applied in Germany.

D. Chemical Storage Systems

The energy density achieved with chemical storage is at least a factor 100 higher than any other storage technology discussed in the previous sections (e.g. see Table 2). This is the decisive advantage giving chemical storage systems unsurpassed competitiveness. Primary energy is predominantly stored chemically in large crude oil and natural gas storage tanks, or as stockpiles or in silos of specific energy carriers like coal or biomass. Secondary or final chemical storage involves refined petroleum products kept in tanks of fuel stations, industries, vehicles, and households. Energy products from coal and biomass like briquettes, granulated coal and wood chips or biomass pellets are kept dry in sheds, cellars, or silos.

1. Coal

Coal is a dark brown to black combustible mineral formed over millions of years through the partial decomposition of plant material subject to increased pressure and temperature under the exclusion of air. Primary coal exists in different grades called anthracite, bituminous and lignite with decreasing heating values, respectively. Secondary coal is produced from primary coal into metallurgical coke, anthracite, bituminous and lignite briquettes. World coal reserves are about 9.1×10^{11} tons, with annual consumption at about 4.5×10^{9} tons per year (Dresselhaus and Thomas 2001).

Table 10: World coal production 1999 [a]

Region/Country	Anthracite	Bituminous	Lignite	Metallurgical Coke[b]
	Thousand Short Tons			
North America	4'768	1'086'789	100'070	26'185
Central & South America	28	49'457	0	10'694
Western Europe	10'308	104'661	380'612	43'499
Eastern Europe & Former U.S.S.R.	35'576	475'221	235'399	66'454
Middle East	0	1'389	0	335
Africa	2'881	324'294	0	5'354
Asia & Oceania	298'961	1'757'120	185'329	214'601
World Total	**352'522**	**3'798'932**	**901'410**	**367'122**

[a] Energy information Administration EIA, DOE, US, http://eia.doe.gov/
[b] Secondary coal; other secondary coal (world wide) are 14'601 t of Anthracite and bituminous briquettes and 11'813 of lignite briquettes

In 1999, coal production was about 5 billion tons worldwide (Table 10). Although production stagnated to this level, coal mining productivity has steadily increased over the last decade [7].

The key environmental drawback of coal mining is the continuous release of CO_2 due to the glow burn of coal floss. Glow burn is impossible to control as oxygen enters the vast underground coal reservoirs during mining activities, leading to self-ignition. Coal combustion releases particulates and the chemical compounds sulfur dioxide (SO_2) and nitrous oxides (NO_x) responsible for the environmental acidification. Pollution abatement equipment is installed in modern plants to control

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[7] IEA World Energy Outlook 2002

these emissions. Together with other essential equipment for coal-receiving, raw coal storage, coal preparation, coal transportation, and space requirements for coal storage result in significantly higher capital investments.

Coal stocks are kept at electric utilities (e.g. in the US 119,000 thousand tons in 2001), or at coke and power plants and other industrial facilities. At coal-handling facilities, crushers and granulators use coal delivered from different coal pits to produce coal fragments of about 50mm in size. The raw coal for power plants or boilers is stockpiled or stored on-site in coal silos. The coal is then taken and crushed in pulverizers into powder to feed the plant's burners. Other coal storage facilities also consisting of coal bunkers, silos, coal strait or stockpile slot systems allow coal from the different pits to be blended and provide short-term storage to accommodate peak shipping demands often performed by railway in aluminum-bodied-car unit trains. Customized solutions to fugitive coal dust problems at ground storage facilities and railroads are often required. Environmental quality control is assured using air quality modeling and monitoring including particulate source inventories, weather observation and forecasting to handle high fugitive dusting potentials, and storm run-off collection and settling pond modeling. In addition, the clean coal technology initiative has lead to pollution control and power generating processes using low sulfur sub-bituminous coal that reduced air emissions from coal burning plants including greenhouse gases [8]. Some of the new technologies offer the potential to use high-sulfur "dirty" coals achieving comparable air emissions. Enhancing power plant efficiencies and capturing carbon gases achieve further CO_2 emission reductions.

2. Crude Oil

World reserves of oil are about $1.6x10^{14}$ L ($1x10^{12}$ barrels) with similar amounts of undiscovered oil resources[9]. World consumption is about $1.2x10^{10}$ L a day. The vast extent of the present oil production from today's deposits is predicted to increase by at least a million barrels every year over the near future. The oil reserves are believed to be economically exploitable for the next 25 years and under the assumption of increasing prices up to about 2040 using improved exploitation technology (Dresselhaus and Thomas 2001).

Believes that crude oil prices will gradually increasing pushing gasoline and diesel prices up, or that more fluctuations of oil prices may occur in the future may find their arguments in possible geopolitical interference affecting fossil fuel supply or in the geological uncertainty to efficiently allocate resources in the future. Having adequate storage capacities help at least to balance short-term price fluctuations. In the long-term, attractive returns on the large investments done by oil firms for exploitations today and in the near future may only be achievable if oil prices steadily rise and additional capital is made available at the right time in order to access these new deposits when needed. But capital may rather be invested into projects with quick returns. OPEC's present oil production and especially today's willingness to prepare for future investments are major uncertainty variables

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[8] Energy information Administration EIA, DOE, US, http://eia.doe.gov/

[9] IEA World Energy Outlook 2002

impacting on future price stability[10]. These long-term uncertainties make any effort to arrive at a valid pricing system of a scarce resource like crude oil impossible (Banks 2000). Storage is no answer for that.

In the short-term, some simple market dynamics can be utilized by primary storage of crude oil, for instance, as to replenish low fuel stocks during mild winters when demand is low for heating oil, or propane and natural gas. Also, an economic slowdown can reduce energy demand and in turn oil prices may decrease as stocks are up. Besides the importance of primary storage for the functioning of the oil market, efficient secondary storage of petroleum products like gasoline, diesel, jet fuel, other (mostly cracked) oil distillates used for heating and other residual oil stocks (light and heavy oil) are crucial for the attractiveness of the energy services based on fossil fuels (Table 11).

Table 11: Example of crude oil and petroleum storage: product stocks[a] from the U.S. in Mbbl (1×10^6 barrels (bbl)[b]

Year/Product	Dec 2001 (Mbbl)
Crude Oil [c]	312,000
Total Motor Gasoline	209,900
Reformulated	*44,900*
Oxygenated	*400*
Other Finished	*116,200*
Blending Components	*48,400*
Jet Fuel	42,000
Distillate Fuel Oil [f]	144,500
0.05% Sulfur and under (low)	*82,300*
Greater than 0.05% Sulfur (high)	*62,200*
Residual Fuel Oil	41,000
Unfinished Oils	87,700
Other Oils [d]	199,100
Total (Excl. SPR)	1,036,100
Crude Oil in SPR [e]	550,200
Total (Incl. SPR)	**1,586,300**

[a] Product stocks include those domestic and Customs-cleared foreign stocks held at, or in transit to, refineries and bulk terminals, and stocks in pipelines. Stocks held at natural gas processing plants are included in "Other Oils" and in totals. All stock levels are as of the end of the period.

[b] Weekly Petroleum Status Report/Energy Information Administration EIA, http://eia.doe.gov/

[c] Crude oil stocks include those domestic and Customs-cleared foreign crude oil stocks held at refineries, in pipelines, in lease tanks, and in transit to refineries. Does not include those held in the Strategic Petroleum Reserve(SPR).

[d] Included are stocks of all other oils such as aviation gasoline, kerosene, natural gas liquids and LRG's, other hydrocarbons and oxygenates, aviation gasoline blending components, naphtha and other oils for petrochemical feedstock use, special naphthas, lube oils, waxes, coke, asphalt, road oil, and miscellaneous oils.

[e] Crude oil stocks in the SPR include non-U.S. stocks held under foreign or commercial storage agreements.

[f] Distillate fuel oil stocks located in the "Northeast Heating Oil Reserve" are not included..

Note: Data may not add to total due to independent rounding.

In many countries oil imports are regulated at least to some extent regarding strategic petroleum reserves (SPR). Compulsory storage ratios are stipulated

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[10] "Short- Term Energy Outlook", DOE's Energy Information Administration (EIA), EIA report, http://www.eia.doe.gov/emeu/steo/pub/contents.html

between importing companies and the government. Often also large consumer companies can join the contracted storage system with the obligation not to empty their stock below a given ratio. SPRs play a key role in the international energy markets stabilizing price fluctuations.

Depending on the annual demand and capital cost of storage and the aging of oil, different amounts of stock are kept by the consumer companies or, regarding heating oil, also by households. Aboveground and underground storage tanks are mostly used also for secondary storage for instance of high or low sulfur distillates. US total fuel distillate ending stock was about 140,000 Mbbl in 2001 with about 40% high sulfur and 60% low sulfur distillates.

a. Oil tanks and the environment

Tanks, some with capacities over 390,000 barrels (over 16 million gallons), store the crude oil, as well as intermediate stocks (partially refined), finished products and chemicals. Thousands of oil storage tanks are distributed over the landscape of oil-rich counties and store the crude oil extracted by pumps scattered throughout numerous oil fields that are sometimes as small as a few acres. Pollution to water and soil often occurs directly through leaking oil tanks. Today, some of oil storage tanks have containment areas designed to hold their capacities in the event of a tank rupture. At refineries such containment system also divert rainwater runoff to the refinery's effluent treating facilities to assure no traces of chemicals or hydrocarbons enter the local waters. However, the crude oil is processed in the fields to separate lighter hydrocarbons and produced waters. This process can lead to methane venting when the crude oil is stored in fixed roof tanks. One possibility to reduce the quantity of methane emissions is to consolidate and centralize the liquid storage facilities in the fields. In the US, regulatory agencies began to develop rules that affected heavy oil storage tanks in order to meet the goals of the Clean Air Act. Reducing storage tank emissions could cost the oil industry tens of millions of dollars.

In addition, about 500'000 leaking petroleum hydrocarbons tanks from secondary and final storage (mostly heating oil and gasoline tanks) have been estimated in the US during the early nineties. The cost of replacement and remediation of contaminated groundwater and soils is estimated to go into tens of billions US$ (Blaisdell and Smallwood 1993).

Today, the petroleum storage tank remediation (PSTR) fund provides reimbursement for remediation of contamination resulting from leaking petroleum storage tanks. A fee on gasoline and other fuels at bulk distribution facilities supports the fund. The fund covers the expenses of corrective action taken in response to a release of petroleum products from a petroleum storage tank, hydraulic fluid from systems located at a vehicle service and fueling facility, and spent oil from spent-oil tanks located at a vehicle service and fueling facility.

Refined petroleum products like gasoline contain sulfur at concentrations ranging from 5 parts per million (ppm) to over 350 ppm and may contain methyl-tertiary-butyl ether (MTBE), or ethanol (EtOH). Due to its recalcitrant properties in the environment, MTBE has been banned in the US to be used as gasoline additive, recently.

From an environmental perspective, all storage tanks should be impermeable to volatile organic compounds (VOC) and should be equipped with pressure-vacuum valves combinable with a vapor recovery system. The emissions of gas built up in

crude oil or produced water storage tanks are controlled during handling by flare combusting of the VOCs or better by tank battery vapor recovery system. The VOC destruction or removal efficiency should be at least 90 to 95 % by weight. External or internal floating roof crude oil tank have vapor space which have to be controlled while the tank's roof is resting on the tank's inner roof supports. The degassing is controlled by liquid displacement into a vapor recovery system, flare, or fuel gas system. An air pollution control device measures the vapor destruction and removal efficiency. Fugitive emissions cannot be completely repressed since tank opening is required for some maintenance operations.

Other innovative methods to store large amounts of petroleum products like diesel have been undertaken in Europe. Investigation of the environmental impact of the underground storage of diesel in igneous rock surrounding underground storage facilities showed penetration into the rock as far as 50 m from the walls of the vaults (Lorén et al. 2001). The major transport of diesel components in rock occurs through fracture systems and diffusion of diesel through the rock. Consequently, the risk for contamination of groundwater cannot be neglected.

2. Natural Gas

World reserves of natural gas are about 1.4×10^{14} m^3; gross production of gas is about 2.4×10^{12} m^3 per year (Dresselhaus and Thomas 2001). In the long-term, i.e beyond 2100, natural gas hydrates from deposits at ocean floors hold a vast tapping potential; even a small part of the potential would already provide a very significant new source of natural gas. Presently, this cannot be exploited economically however[11].

The consumption of natural gas varies daily and month-to-month along with changing weather conditions and with the demand for electricity generation. Seasonal fluctuations are as much as 50% and in the short-term more extensive variations can be observed. Place and volume of peak-demand is unpredictable and therefore exact timing impossible without integrated storage systems. Natural gas production does not correspond to these fluctuations; surplus gas is pumped during low-demand into numerous mostly underground storage facilities for use during high consumption periods.

To enhance pipeline performance, natural gas is stored in two basic ways – compressed in tanks as liquefied natural gas (LNG) or in large underground storage facilities. This allows continuous service even when production or pipeline transportation services do not meet short time capacity needs. Underground storage systems are artificial deposits of injected natural gas in porous rocks of depleted fields or aquifers, or in artificial underground caverns like abandoned mines or salt caverns. By far the greatest volume of gas is stored in depleted gas wells or salt caverns as primary storage (Table 12). LNG is kept as chilled and pressurized liquid in double walled cryogenic vessels or tanks. Typically, natural gas is moved as gas through pipeline systems. Transportation by ships or trucks is done in its liquefied form. LNG requires 600 times less storage space than its gaseous form and the ability to ignite is strongly reduced. In the US however, LNG plays only a small role on the gas market, because of extended pipeline systems being available. Used

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[11] EIA, 1998 Natural Gas: Issues and Trends

as vehicle propellant in combustion engines, natural gas is kept in tanks as compressed natural gas (CNG) on-board of vehicles and at filling stations. Volumetric capacity depends on head and shell thickness of the storage vessel.

Table 12: Example of natural gas storage: primary storage in the US for the year 2000[a] in volumes of billion cubic feet at 1 bar pressure and at 15 degrees Celsius.

Traditional Storage	Salt Caverns	Total
5,927	145	6,072

[a] EIA, Natural Gas Monthly, (March 2001), http:// www.eia.doe.gov/oil_gas/natural_gas/ nat_frame.html

Well functioning storage systems eliminate the need for expensive, additional pipeline transmission capacity that would be necessary to supply peak-demand. For instance in the US, excess production of natural gas is injected into approximately 410 storage reservoirs that account for almost 4 trillion cubic feet of storage capacity, (over 15% of one year's national gas consumption). This storage system allows consistent delivery of the natural gas resource to consumers having stabilized supply by using summer production levels for shortages in the winter.

Increasing demand, changing demographics and the deterioration of storage and pipeline systems impose technological challenges for the future of the gas markets. The use of natural gas is projected to increase at a rate of 2% per year for the next 2 decades due to ongoing decarbonization trends of fossil fuels, e.g. using natural gas rather than petroleum and diesel for combustion engines or oil for heating purposes[12]. During this time, there will be a significant shift in consumption patterns as the population of many countries accustoms to more natural gas for the generation of electricity to power air conditioning, or for heating, cooking and mobility.

Present storage wells must be renewed or replaced as older storage areas experience "wear" due to the yearly cycles of injection and extraction of gas. Innovative methods to enhance operational flexibility of the nation's gas storage system are requested while ensuring the integrity, operational reliability, safety and security of the natural gas infrastructure.

a. Underground storage and liberalized markets

The dependence on imports and occurrence of bottlenecks within gas transmission grids requires a competitive way to cover gaps between transportation capacities and withdrawals. Underground storage facilities are localized near consumption areas, in order to raise the deliverability of the network. They allow decreasing the total amount of investments in infrastructures. A gas pipeline network is composed of many supply and demand nodes, pipeline links that tie together the supply and demand sides, and corresponding storage sites for LNG.

The liberalization of energy markets aims to separate network infrastructures and energy services. Supply is liberalized while buyers and sellers are allowed to use the existing gas grids operated by regulated natural monopolies. More open gas

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[12] EIA, 2002 National Energy Technology Laboratory, U.S. Department of Energy, http://www.eia.doe.gov/

markets force on competition and trading, and install more pressure on demand balancing and price volatility. Basic conditions for a future, well functioning gas market are security of supply, long term planning of investments and equity of access to the grid. Underground storage can play a major role in this gas chain, especially for remote areas, where improvements of natural gas services using pipelines with the capacity needed for peak demand are too expensive.

b. Natural gas and mobility

While natural gas vehicles (NGVs) have penetrated some niche commercial markets for buses, delivery vans, and trucks, their success is still heavily constrained by the cost, weight, and size of existing natural gas storage cylinders. In the 90ties, a state-of-the-art, safety-certified natural gas storage unit called the Integrated Storage System (ISS) has been developed. The ISS utilizes lightweight, high-density polyethylene to construct small diameter cylinders (called pressure cells), which are subsequently encapsulated within a high- strength fiberglass shell containing impact-absorbing foam. The ISS is easily integrated into common vehicle chassis. The separation into two tanks, for instance one on the undercarriage and one located in the trunk, provide a total energy storage capacity of 45 liters of gasoline equivalents at a service pressure of 250 bar leading to an automobile driving range of over 480 km comparable to those powered by gasoline. ISS technology innovation reduced the cost of NGV storage tanks by nearly 50%. Its weight savings is up to 70% as compared to steel and aluminum cylinders, and ISS does not interfere with the car's crumple-zone. Daimler Chrysler has tested the ISS in several sedans and reported very positive results. However for commercial viability cost of natural gas storage must still be significantly reduced. Further development of composites for cheaper and lighter weight ISS components is underway[13].

4. Hydrogen

Hydrogen is presently used mostly as chemical feedstock in the petrochemical industry, and in food, electronics and metallurgical processing industries. Hydrogen is however believed to have a great potential to be used as major energy carrier for clean energy systems in the future. A society powered almost entirely by hydrogen, the most abundant element in the universe, is a strong vision for the future. Hydrogen can be used in transportation, buildings, utilities, and industry, and can be used as chemical storage compound. For instance, renewable resources like wind and solar power can be used to extract hydrogen from water with the only emission of oxygen. The intermittency of renewable resources can then be balanced by hydrogen combustion reforming water. One of the technologies that can be used for conversion is the fuel cell (compare chapter B). Hence hydrogen is complementary and not competing with the renewable conversion technologies.
When hydrogen is used as an energy source, it ideally generates no emissions other than water. It would therefore strongly contribute to the reduction of energy-linked environmental impacts especially regarding anthropogenic emissions into the atmosphere. If combined with decarbonization technologies, hydrogen can be used

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[13] Kevin Stork, Office of Transportation Technologies, John Wozniak, Johns Hopkins Applied
    Physics, Laboratory, and Dale Tiller, Lincoln Composites

for upgrading carbon-rich fuels like biomass and some solid and liquid fossil fuels, to less carbon-intensive fuels and therefore support CO_2-emission mitigation. Making the hydrogen vision a reality in the 21st Century is the goal of many researchers at universities and industries which have started to align their efforts internationally (IEA 2000).

a. Hydrogen for mobility

Although little energy is needed to sustain movement, much is lost through friction (for cars about 10 kWh per 100 km) and low-efficiency energy conversion. Therein weight is a problem aggravated by additional weight from on-board fuel storage. Although new battery technologies are developed, so far batteries have not shown to be an ideal option for motor vehicles. For vehicles that store energy on board, hydrogen would be ideal as a synthetic fuel because it is light, highly abundant and its oxidation product is water, an environmentally benign compound. Hydrogen as energy storage option for mobility is gaining more and more attention (see section b).

For example, a centralized hydrogen generation plant powered by solar photovoltaic, with compression and storage facilities could be the start for an infrastructure to support mobility based on hydrogen[14]. The system consists of a stand-alone electrolyzer, hydrogen dispensing system powered entirely by photovoltaic energy, and is combined with an on-site storage tank for solar hydrogen. The hydrogen fuel on the vehicles is stored in carbon composite tanks at pressures up to 250 bar providing fuel for 140 miles. If the engine operates in lean burn mode, no CO and hydrocarbon emissions, and only low NOx emissions (10 to 100 ppm) are exhausted by the vehicles; an effective strategy for improving urban air quality (Provenzano et al. 1997).

Further developments are directed towards hybrid zero-emission vehicle using hydrogen lean-burning spark-ignited engines in different configurations with flywheel, supercapacitor or batteries as energy storage devices (Aceves and Smith 1996). Continued technology development and cost reduction promises to make mobility based on hydrogen competitive.

Another demonstration of a hydrogen support system is the regenerative energy storage systems for ultra-high-flying solar aircraft. The system is designed to store energy by converting the craft's excess solar power into hydrogen and oxygen during the day, and then to use a fuel cell to "regenerate" electricity at night (NASA, 2002)[15].

b. Hydrogen storage research

Hydrogen storage necessary to continuously fuel automobiles or fuel cells is a major safety problem. Today, hydrogen is stored as a compressed gas for example in vehicles, or a cryogenic liquid in physical storage systems for transport. Solid-state storage systems is another, safer storage technology that could potentially store more hydrogen per unit volume. Solid-state systems bind hydrogen to a solid material like carbon. Critical parameters for solid-state storage are hydrogen uptake capacities, controlled hydrogen release and rapid hydrogen refilling. Potential

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[14] The Clean Air Now (CAN) Solar Hydrogen Project, Xerox Corp., El Segundo, California, USA

[15] http://www.dfrc.nasa.gov/PAO/PressReleases/2002/02-24.html

advantages of solid-state storage are the applicability under reasonable operating conditions like higher temperatures and near ambient pressures. Presently, metal hydrides are the most promising materials for hydrogen storage, especially the lightweight metal alloy hydrides (Schlapbach and Züttel 2001).

Despite the interest and activity in solid-state hydrogen storage research, no breakthrough is yet in sight (Dresselhaus and Thomas 2001). However, based on the experience of the industrial gas industry and of chemical process engineering on space technology different methods of hydrogen storage have been proposed and partly investigated in the past. On-board fuel tank storage system depends on the kind of vehicle and the mode of its operation. The introduction of natural gas powered vehicles benefits the efforts to develop hydrogen technology as well (Ewald 1998).

5. Biomass

Biomass fuels (biofuels) utilize the chemical energy fixed by photosynthesis and stored within plants. This chemical energy released as heat by combustion, i.e. burning briquettes, pellets or wood chips, is used for space heating mostly, or for producing industrial process heat. The heat can also be converted to electricity using steam turbines. Instead of producing heat directly, gaseous or liquid fuels like methane, hydrogen, alcohols, or biooils can be produced from biomass. As alternatives to petroleum-based fuels, both liquid biofuels (e.g. biodiesel) and biogas are applicable in internal combustion engines or fuel cells. The conversion of biomass to electricity is conceptually similar to the conversion of coal to electricity by direct combustion or gasification. Biomass is currently also converted to liquid fuels by fermentation of carbohydrates to ethanol, or by extraction and refining plant oils. Gaining significant market shares would require large cost reductions and efficient biomass conversion technologies. Therefore, the main activity today is to further explore ways to reduce the costs of liquid/gaseous biofuels delivered by specific renewable energy technologies.

Only a fraction of the biomass today is harvested and used in current technologies. Besides growing and harvesting biomass, significant amounts of energy are consumed in producing biofuels. About 6% of the (lower) biomass heating value is used per unit production. Fertilizing (production, transport, application), irrigation, and harvest, transport and preparation (wood chips as example) consume more than 75% of the biomass production energy, while fertilizer production alone accounts for 35%. Developments to improve the overall efficiency of a biomass energy system are very important tasks for the decade to come. Land requirements however remain a distinct characteristic of this renewable energy source. Biomass energy production depends on the availability of suitable land and water that varies by region. As the extent of crop yield increase for food, timber, and fiber crops, the land becoming available competes for settlements and corresponding infrastructure and industry.

From an environmental perspective biomass combustion can lead to significant emissions of air pollutants if no adequate control measures are installed. Burning wood or wood chips, for example, generate sulfur oxides, nitrous oxides and lots of particulates (e.g. PM_{10}) and many trace chemical pollutants. Modern equipment can reduce these emissions to some degree by using optimized air to fuel ratio, temperature control and raw material, innovative combustion chambers, and filter

systems especially for larger, around 1-5 MW power plants. Also biomass gasification has a cleaner technological potential for directly generating biogas. Biogas can be distributed over the gas grid or used in internal combustion engines. Overall energy balance with regard to CO_2 reduction potentials of biogas production routes or enzymatic conversions of biomass to ethanol could become significant. But a sustainable production has to be based on a highly efficient management of energy crops. This includes short rotation coppice, use of waste recovered fuels, and an integrated view on the complete bio-fuel chain from growths to the logistics of harvesting, drying, and delivery, not to forget the marketing and distribution of energy products.

Plants on land are not the only option for renewable biomass production. Marine algae, including kelp, are potential renewable resources. Annual micro-algae productivity at saturating levels of CO_2 is estimated as high as 81 dry-tonnes per ha and year (36 tC ha^{-1} year^{-1}). Cultivated macro-algae, like kelp, are reported to have yields of up to 150 dry-tonnes ha^{-1} year^{-1} (Kheshgi et al. 2000). The yields seem significantly higher than for sugarcane under optimal conditions. Large-scale exploitation of micro-algae is done mostly for food additives, as energy resource exploitation is currently too expensive.

a. Biomass energy stored in plants

Sunlight reaches the Earth's surface with an annual average energy density of 180 W/m^2. Theoretically, about 6.7% of the solar energy input on land could be converted to chemical energy by photosynthesis, although on average only 0.3% is stored as carbon compounds in land plants. The global plant biomass is estimated to be about 600 GtC on land, and only about 3 GtC as marine biomass. Net primary productivity (NPP), is about 60 GtC per year on land, and 50 GtC per year at sea (Kheshgi et al. 2000). Biomass varies somewhat in both its energy and carbon content having different heating values. Poplar or other fast growing crops have energy contents around 15 to 20 GJ/dry-t.

b. Biofuel storage

Primary biomass storage includes any organic matter available on a renewable basis, including dedicated energy crops and trees, agricultural food and feed crops, agricultural crop wastes and residues, wood wastes and residues, aquatic plants, animal wastes, municipal wastes, and other waste materials which are logistically harvested, collected or stored for supporting a continuous biomass resource supply chain to produce biofuels, or other bioliquids and synthesis gases (Syngas).

One major issue in secondary or final storage of biofuel is the oxidative stability of the compounds. Stability test methods are developed to allow a customer to determine if the fuel will remain stable in storage over extended periods of time. In general, high acid numbers coupled with high viscosity numbers indicate a degraded liquid biofuel. For solid fuels, security measures to prevent (self-)ignition in the presence of heat and oxygen are important.

i. Biogas

Biogas is the most promising biofuel. Compared to liquid biofuels, it is more directly accessible, has better overall energetics and can be applied more flexibly. It can be produced by fermentation processes, pyrolysis or gasification techniques from many different biomass raw materials, ranging form wood, forest residues,

agricultural plant residues, manure, organic waste, and sludge. Gasification is possible for raw materials carrying less than 50% moisture. Biogas from 1 kg of air-dried, gasified biomass stores about 8000 kJ energy, which can deliver about 0.8 kWh electric output. Biogas production from biomass pyrolysis is taking place at high temperature, under exclusion of oxygen, and in the presence of catalysts. Both techniques are also used as intermediate step in the production of methanol and ethanol.

Biogas storage is no different than the storage of natural gas discussed above. Larger quantities are stored in standard gas storage tanks, tanks with inflatable rooftops, or double membrane storage tanks holding the gas at constant pressure. Since biogas contains hydrogen sulfide, tank materials must be H_2S-resitient. The purity of biogas as compared to natural gas is a remaining issue, which adds to the controversy in debates about the economic feasibility of large biogas production plants. In addition, challenging aspects of catalysis important for fermentation, gasification, or pyrolysis, require enduring research and development efforts.

ii. Biofuel ethanol

Alcohol production through microorganisms is one of the oldest roots of biotechnology. Biomass is converted to a fermentation feedstock, where microorganisms including yeast and other bacteria produce ethanol in a relatively dilute aqueous solution. The biomass comes mostly from corn. For biofuel production, its fermentation yields fuel-grade ethanol, heat and some byproducts in an aqueous product solution. 1 L of ethanol is gained from about 2.6 kg of corn. Alternatively, gasification of biomass at high temperature yields gaseous intermediates like hydrogen and carbon monoxide used as precursors for ethanol production. For example, anaerobic bacteria can be used to convert the CO, CO_2, and H_2 into ethanol. Still, ethanol must be isolated from the aqueous product solution by distillation, which uses most energy in the process chain. 1 liter of 95% ethanol is received after 3 distillations leaving 124 l of water behind.

Blending of gasoline and ethanol to produce a form of alternative transportation fuel has gained al lot of support in the U.S. For blending, the 95% ethanol must be further processed with more energy inputs to achieve 99.8% pure ethanol. Presently, the blended vehicle fuel E85 contains 85% ethanol. With E85 having less energy content than gasoline, new incentives intend to "equalize" the cost comparable to conventional gasoline. Product storage of ethanol takes place at the product terminals where gasoline and ethanol are blended. The gasoline arrives at the terminals via pipeline, barge, or ship while the ethanol arrives by truck, rail, barge or ship. Each is stored in its respective tanks until drawn from stock, for blending in ethanol. The size of the ethanol tanks must be compatible with the blending program with its projected ethanol demand. The tanks also function as reservoirs and must be large enough to receive the minimum shipment size without having to deplete safe working stocks. The estimated cost of installing a 25m-barrel tank is around US$ 450,000.

Ethanol is a regional product and is made out of agricultural produce, especially corn. Added to gasoline it would extend supply and also would enhance agricultural profitability while being a renewable resource. However, its reduction of the dependence on foreign oil is controversial.

iii. Biodiesel

Biodiesel is the transformation product of long-chained fatty acids from renewable lipid sources to the corresponding mono alkyl esters. Biodiesel is typically produced through the reaction of a vegetable oil or animal fat with methanol in the presence of a catalyst to yield glycerine and methyl esters. Another catalytic process is the direct reaction of a fatty acid with methanol to methyl ester.

Biodiesel is used as alternative fuel especially in agriculture either in neat form, or blended with petroleum diesel for use in compression ignition (diesel) engines. Its physical and chemical operation properties are similar to ordinary diesel fuel. Interesting properties of biodiesel are the absence of sulfur or aromatics, and the increased lubricity. The interaction between biodiesel and the accumulated tank sediments and sludge from ordinary diesel reduces the solvency problem of ordinary diesel. The "clean out" tendency of biodiesel carries increasing amounts of dissolved sediments into the fuel systems of the vehicle where fuel filters catch most of it. This tendency is the most innovative characteristics usable also for oil tank clean up. But biodiesel is a natural solvent which softens and slowly degrades certain types of elastomers and natural rubber compounds, e.g. of fuel hoses and fuel pump seals.

Biodiesel can be stored in standard diesel storage tanks. Copper, brass, zinc, lead, and tin parts should be replaced with aluminum or steel since these metals oxidize both diesel and biodiesel fuels and create sediments. Besides aluminum and steel, acceptable storage tank materials are fluorinated polyethylene, fluorinated polypropylene, and Teflon (Howell and Weber 1996). Biodiesel blends do not separate easily in the presence of water; yet, biodiesel tends to freeze at higher temperatures than other types of diesel.

Similar to ethanol, a sustained biodiesel market would also provide direct benefits to the agricultural sector. For instance, a strong demand for biodiesel also as lubricant and clean out agent could add additional value to soybean production. However the major problem is its economics and the negative energetics of the biodiesel production.

E. Conclusions

According to the thermodynamic laws of physics an efficiency loss is unavoidable for all storage systems. Nonetheless, the capacity and services of energy systems, including load distribution or system reliability, must continually be optimized. Load distribution strategies and energy end use efficiency increase customer benefits, while energy storage and control devices allow consumers to time energy purchases and shift from high to low rate periods. Energy storage also increases system reliability and will be the key to balance the intermittency of new renewable energy sources in the future.

Efficient electricity storage in larger quantities is only indirectly possible by using established storage techniques like pumped storage hydropower plants pumping water back to the reservoir at times of low electricity demand. This established storage technique could become even more important in the future. However, for such large systems, the foremost limiting factor for future growth is the availability of suitable sites with low environmental impact. Similarly, the development of large-scale CAES will depend on developing systems with man-made storage tanks. Over the last twenty years, smaller scale electricity storage technologies have progressed greatly. New energy storage systems involving flywheels are very promising especially in combination with other storage technologies to support uninterruptible electricity supply systems, thus improving reliability and quality. Batteries remain significant for smaller appliances and applications where grid power independence is necessary. Supercapacitors have been developed as an additional electricity storage technology to maintain grid stability and satisfy rapid power needs. Increased capacity in electricity storage including the sum of all smaller-scale technologies will be required as the level of electricity generation from intermittent renewable energy sources increases.

Thermal storage technologies are especially useful in combination with solar energy, CHP, and waste heat distribution to provide hot water and heat for housing. Although large thermal storage systems like HT-UTES and ATES are more efficient, small-scale applications intelligently integrated into building technology have immense potential. Interesting examples are the use of PCMs and Zeolites in heating, cooling or ventilation systems.

Chemical storage still remains the definitive storage method with its high energy density. The use of coal and oil however, poses great problems for sustainable energy due to CO_2-emissions. The transition to natural gas, hydrogen and biomass as prime chemical energy storage is envisaged for the future. Cost reductions in the various chemical storage techniques will be crucial for applications in mobility, distributed electricity generation, and heat production.

Energy storage should be lean, safe and reliable to contribute to the well-functioning of energy supply markets and energy systems. Some redundant capacity of energy storage is important for all sectors of the socio-economy to cope with disruptions caused by various technical, economical, or political events

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