
Resource, recycling and waste challenges for storage resources in a 100% renewable economy

Senior Thesis – Chemical Engineering, B.Sc.

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Abstract

In this thesis, the battery storage needed for a 100% renewable economy was calculated. It was determined that the use of batteries as a worldwide energy storage solution is not viable. Other systems, such as power-to-gas, would undoubtedly be a better match, as they are much less resource-intensive, and they could be combined with the existing natural gas infrastructure for lowered costs.

Data was gathered for two regions that would be studied in detail. These regions were (1) Germany, Austria and Luxemburg, and (2) California. An in-depth analysis of the load and renewable generation (from solar and wind) profiles was done, which was used to calculate the amount of battery storage that would be needed in the area, as well as the requirements that an electrolyzer should be able to meet. Data was also gathered for the world, which enabled a study about consumption, generation and current renewable capacity, among others. Solar irradiation and wind maps were used to estimate the potential of each of the renewable sources studied to provide energy in the scenario of a 100% renewable economy. A theoretical approach about electrolyzer technologies, batteries and practical aspects of hydrogen as a gas fuel can also be found in the thesis.

The available data for the two regions studied, along with the results of their storage calculations, was used to calculate the fraction of energy that was provided by each of the renewable sources studied. With this information, an equation was obtained and used to calculate the storage needed for other regions in the world if their approximate renewable potential (fraction) and consumption were known. The estimated total energy storage for the world was then calculated considering each of the continents and was found to be a total of 19,981 TWh (100% roundtrip efficiency – ideal battery). Since the average energy density of batteries is known, it is estimated that this amount of storage would require a 133,205 Mt battery, and since the estimated composition of lithium-ion batteries is also known, it was calculated that to build such an amount of storage would be quite resource-intensive: 3,143.64 Mt of lithium and 25,815.13 Mt of cobalt. If the reader takes into consideration that the lithium and cobalt reserves are estimated to be about 53 Mt and 145 Mt, respectively, it is easy to see that the calculated amounts required for the battery are, by far, too large to be executed.

Due to the low cost of extracted lithium, the fraction of the metal used today that comes from recycling is scarily close to zero. Most of the recycling processes for lithium are currently only at research stage, and the majority of them combine physical (battery dismantlement and crushing, along with physical separation of compounds) and chemical processes (leaching, extractions, precipitations), the latter being the ones that have traditionally been used in the mine industry to extract metals (hydrometallurgy). They use harsh chemicals that can be cleaned and reused, and finally sent to a dedicated treatment plant as it is done in the chemical industry.

These results were obtained by means of gathering and analyzing data on energy consumption and generation profiles, and considering renewable capacities for solar and wind, in the case of the specific regions; considering information on global and continental-based energy consumption and generation amounts, and renewable potentials for the worldwide estimations; and studying the composition and characteristics of the lithium-ion batteries used today, along with the available critical metals reserves, to calculate the amounts of resources that would be needed to fabricate the calculated energy storage devices.

Goals and objectives

The goal of the thesis is to **determine the magnitude of energy storage required for a 100% renewable economy and analyze the resource availability, recycling potential, and waste challenges associated with popular energy storage technology options.**

To meet this goal the following set of objectives is developed:

- Objective 1. Do a comprehensive analysis of the power demand needed by two certain locations for an entire year, including total amount of energy needed, seasonal, diurnal, and hourly dynamics.
- Objective 2. Determine the amount of renewable energy (solar, wind) and local availability of such in the locations studied in objective 1.
- Objective 3. Calculate the energy storage (battery) sizes that would be necessary to satisfy the load and handle the annual dynamics.
- Objective 4. Based on the obtained results, estimate the amount of energy storage that would be needed at a worldwide level.
- Objective 5. Determine whether resources are sufficient to produce all of the required energy storage systems.

Approach

1. Gather & analysis information about the performance.
 - a. Data about the energy profile that needs to be met.
 - b. Data about renewable energy generation profiles.
 - c. Sizing of battery.
2. Analyze environmental repercussions.
 - a. Needed resources to manufacture.
 - b. Life cycle.
 - c. Recycling issues & challenges.
3. Discussion about choices.

Part 1: Worldwide energy demand and renewable resources

1.1. Introduction: the lithium-ion battery

Presented to the market in 1991, the applications of the lithium-ion battery range from consumer electronic devices to industrial energy storage [1]. A battery is composed of several electrochemical cells that are connected in series and/or in parallel to provide the required voltage and capacity. The amount of electrical energy that a battery is able to deliver is a function of the cell potential (V) and capacity (A·h/kg), and can be expressed either per unit of weight (W h/kg) or volume (W h/L) [2]. A detail to take into account is that the term *lithium-ion battery* refers to any battery that uses lithium as a charge carrier and its functioning is based on insertion reactions in both of the electrodes, which includes many types of cells. The cell is structured in an anode, cathode, and separator architecture, with the addition of an electrolyte, which allows ionic transport between the electrodes [3]. The physical design can come in various forms, some of which can be observed in Figure 1.

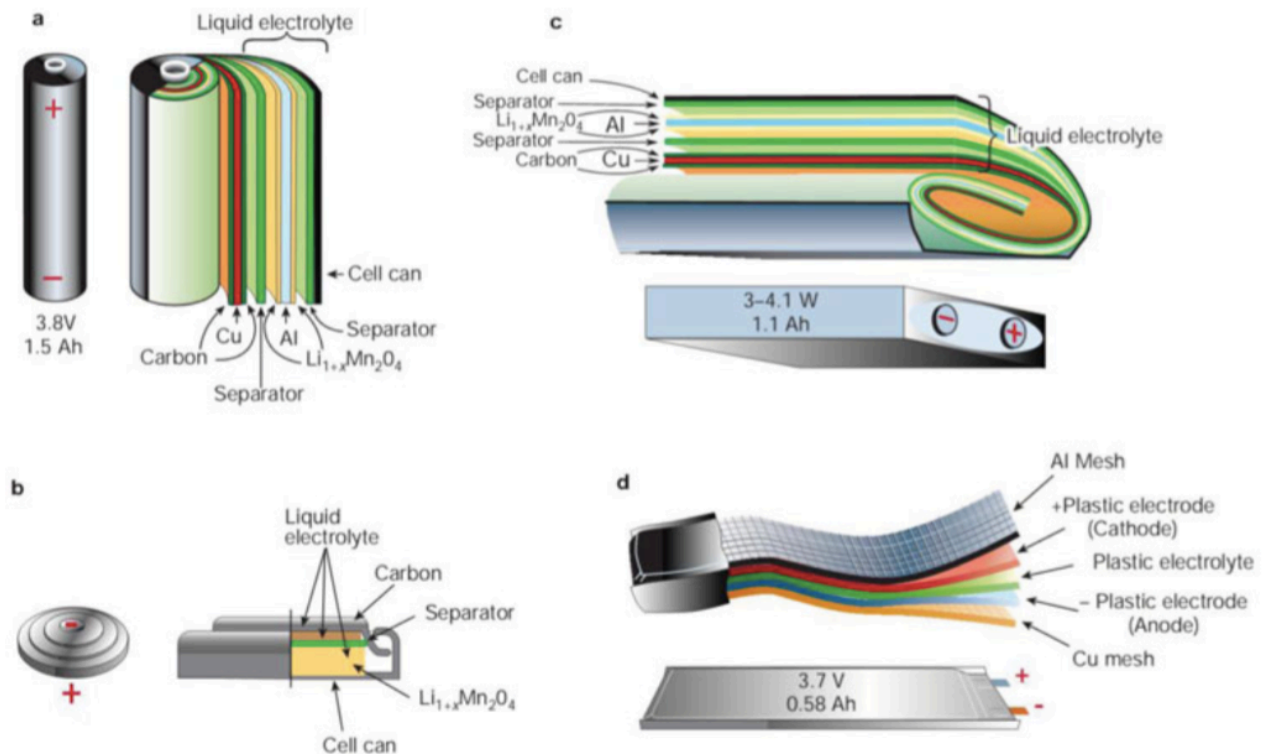


Figure 1. Various LIB configurations. a: cylindrical, b: coin, c: prismatic, d: thin and flat. Source: *Issues and challenges facing rechargeable lithium batteries*, Tarascon, J.-M., Armand, M., 414, 2001, Nature, 359-367.

In commercial batteries, the anode is made of carbon, in the form of graphite, hard carbon or soft carbon, or lithium titanate (Li₄Ti₅O₁₂). The lithium source for the reactions is provided by the active materials of the cathode. The first compound used for this purpose was lithium cobaltate (LiCoO₂); later, compounds with the general formula LiM_xNi_{1-x}O₂, where M is a metal element different from nickel, such as cobalt (Co), manganese (Mn), aluminum (Al) or magnesium (Mg), were –and currently are– used, as well as lithium manganese oxide (LiMn₂O₄) and lithium iron phosphate (LiFePO₄). A lithium salt dissolved in an aprotic

polar organic solvent is used as an electrolyte [3]. The separator is typically a microporous polymer membrane, which allows the exchange of lithium ions between the two electrodes, but not of electrons [4].

Nowadays batteries are manufactured in a discharged state. Once they are assembled, they are charged. In the charging process, the two electrodes are connected to an external electrical supply. In this state, the lithium ions move from the cathode to the anode via the electrolyte, while the electrons flow in the same direction in the wires outside the battery. When the battery is discharging, the process is reversed [4].

One option that is being considered in order to extend the lifecycle of batteries is changing its placement. The idea is that after a certain period of use, their performance will be affected, and while a battery that was used to run a car may no longer be useful for that purpose, it could still serve in a house, where the availability of an electrical source to be recharged is located conveniently near. Recycling procedures to treat the batteries when their lifecycle comes to an end are being studied but are not yet implemented in an industrial level. However, an increasing pressure is being applied in this particular area, since batteries contain heavy metals and so they are considered hazardous for the environment. The main focus of the recycling processes is the recovery of the expensive metals used (Co, Ni, Li). The processes being studied can be classified in chemical and physical processes, though a combination of the two is most often used [5]. These processes will be discussed in the dedicated chapter of the thesis.

In 2000, the worldwide production of LIBs reached about 500 million cells. Based on this consumption, LIBs waste is annually estimated at 200-500 million tons (MT), the metal content of which is about 5-15% Co and 2-7% Li (in weight). Between 2000 and 2010, the annual production of LIBs increased by 800% in the world. Due to the electric vehicle industry market growth, it is estimated that the quantity of this type of batteries that will be discarded by 2020 can surpass 25 billion units, or 500 thousand tones. The total lithium demand is also expected to go through a remarkably important growth, from 0.3% in 2010 to 40.3% [1].

1.1.1. Definitions

- **Hydrometallurgy.** Technique or process of extracting metals at ordinary temperatures by leaching ore with liquid solvents [6].
- **Primary cell or battery.** A battery that cannot be recharged and so it is discarded after discharge.
- **Secondary cell or battery.** A battery that can be electrically recharged, meaning that they can be reset to their initial condition by passing current through the circuit in the opposite direction to the current during discharge [7].
- **Resource.** “A concentration of naturally occurring solid, liquid, or gaseous material in or on the Earth’s crust in such form and amount that economic extraction of a commodity from the concentration is currently or potentially feasible” (USGS) [8].
- **Reserve.** Part of an identified resource that meets specified minimum physical and chemical criteria related to current mining and production practices, including those for grade, quality, thickness, and depth, and that are considered to be economically available at the time of determination [8].

1.2. History of batteries

The Italian physicist Alessandro Volta found, in 1800, that two metals separated by solutions capable of conducting an electric charge could be arranged in a way that a new charge was created as fast as the old charge was carried off along a conducting wire [9]: the first battery had been invented and, with it, electricity started to be something reliable. Electricity had been long known, though. In fact, static electricity was discovered around 600 B.C. in Greece, because a curious characteristic of amber called the attention of people: when rubbed with cloth, amber would, through some invisible mechanism, pull feathers toward itself. The phenomenon resembled magnetism, but more than two millennia would have to pass before human understanding of these two forces advanced appreciably. Amber was called *elektron* in Greek, which is where the word electron came from [10].

The oil crisis of the 70s motivated the worldwide automobile industry to focus their research into electric driving and advanced batteries to replace fossil fuels. The idea of using lithium batteries had come up in a conference. The major companies, including important oil companies, were soon researching about them. Exxon –oil giant– created, between a few burning accidents, the first lithium battery that worked at room temperature, which was also rechargeable: the Whittingham battery. The device was based on sulfides; more specifically, in LiTiS_2 . The first paper about it was published in 1976, in *Science* [10 págs. 28-31]. When the recession of 1979-1980 arrived, Exxon and everyone else changed into survival mode. Exxon sold everything that had to do with batteries, and went back to oil. During the oil crisis the hunt for new reserves had also been on the go, and they had actually been found: as a result, all interests in developing alternatives to oil were lost [10 pág. 36].

In 1976, Goodenough started working on the development of a new battery. He knew that using lithium oxides instead of sulfides would reach a higher voltage. After getting an idea from an undergraduate thesis that reminded him about some research on lithium nickel oxides he had done back in the 50s, he told his postdoc student to test chromium, cobalt and nickel (LiMO_2), and see how much lithium he could take out before the compound became unstable, which means, see what kind of voltage would each substance deliver in a battery. With the results, he built a discharged battery, rather than charged, as it had been done until the date. This meant that compounds that were stable at room temperatures could be used. At the time, no one showed interest in the invention, and it would have to wait for years before it seemed attractive to someone [10 págs. 43-44].

In the late 80s, Tozawa's team from Sony figured out how to make a lithium-ion battery safe and cheap enough for large-scale manufacturing: a carbon anode and Goodenough's cobalt cathode. It had a nominal voltage of 3.6V, which was quite an achievement, considering that the batteries that were being used at the moment (nickel cadmium, which came out in 1990) had a voltage of 1.2V. It would also last longer because the reaction it relied on was extremely reversible, and so this kind of battery would not suffer from the "memory effect". They were called lithium-ion batteries to distinguish them from the lithium batteries that created Exxon in the 70s and which were known for bursting into flames [10 págs. 49-50]. Some safety tests were carried out, a patent was filed and the design enabled large-scale manufacturing of Li-ion batteries to begin in the early 90s [4].

General Motors executives argued that, thanks to the lithium-ion battery, the time for the electrification of the automobile had arrived. Lead-acid batteries were too heavy and inefficient, bulky and short-lived [10 pág. 5].

1.3. Power-to-gas: A theoretical approach

The forthcoming of fossil fuel resources coming to an end forces researchers to look for alternative and viable energy sources. Renewable energy sources –solar and wind, among others– have been in operation for some years, but since they highly depend on non-controllable factors, they are not as reliable as needed, for it is likely that the energy profile they produce does not meet the demand of the load at every given moment. Consequently, if these systems are used by themselves, there will be moments when the energy they provide is not sufficient to meet the demand of the load, as well as spans of time when a lot of energy is being produced but not utilized, and thus, lost. That is where energy storage technologies come into the game. Current energy storage technologies include electrolyzers, which follow an increasingly popular concept: power-to-gas—a term which describes the conversion of surplus renewable electricity into a fuel, it being hydrogen or methane, using electrolysis–, and long-known batteries.

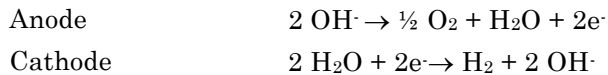
The idea behind power-to-gas (derived from the German “Strom zu Gas” [11]) is to use electrical energy to obtain a gas fuel. This objective is met by means of water electrolysis. Even though it has mostly gained popularity in the early past years, the history of electrolysis actually begins shortly after the first industrial revolution, in 1800. The Italian physicist Alessandro Volta had just created the first battery, thus discovering that a chemical reaction could produce electricity. With this newly acquired knowledge, it did not seem so farfetched to suppose that an electric current could produce a chemical reaction. Within six weeks of Volta’s first description of his work, two English chemists, Nicholson and Carlisle, decomposed water into hydrogen and oxygen by means of electricity [9] [12]: the first water electrolysis had taken place. By that time the molecular formula of water was not yet known, and when hydrogen and oxygen were trapped in separate vessels as they bubbled off, it turned out that the volume of oxygen produced was half the volume of hydrogen produced. Considering these results, the English chemist Dalton [13] proposed that the water molecule may be formed by two hydrogen atoms and one of oxygen [9]. By 1902, more than 400 industrial water electrolyzers were in operation. In 1939, the first large water electrolysis plant went into operation, with a capacity of 10,000 Nm³ H₂/h. In 1948, the first pressurized industrial electrolyzer was built by the hand of Zdansky for Lonza [12].

This concept is becoming increasingly popular today due to a variety of motives: the forthcoming of a shortage in fossil fuels, getting improved energy and economic security by reducing dependence on foreign energy supplies, increasing affordable domestic energy supplies to meet anticipated demand and reducing air pollution and addressing concerns about climate change among them [14].

1.3.1. Electrolyzers

In the electrolyzer, water is split into hydrogen (H₂) and oxygen (O₂). This reaction is not spontaneous and needs energy to take place, which is provided as direct current. To produce a standard cubic meter of

hydrogen, theoretically 3.54 kWh are needed. This value corresponds to the upper heating value¹ of hydrogen. Electrolysis is a reduction-oxidation (redox) reaction. Hydrogen is formed as the product of the reduction half-reaction, which takes place in the cathode; oxygen is formed as the product of the oxidation half-reaction, which takes place in the anode.



The cathode and the anode are separated to assure that the products formed do not recombine again to form water back, and the charge equalization occurs in the form of ionic conduction through an electrolyte. A basic diagram of the structure of an electrolyzer can be observed in Figure 2. Upscaling electrolyzers is quite simple because of their modular nature: they are formed by a stack of cells connected in series.

There are three basic types of electrolyzers: alkaline electrolyzers, proton-exchange membrane (PEM) electrolyzers, and high temperature electrolyzers [15 págs. 290-291]. Among the options that are found in the market for energy storage, electrolyzers and batteries are the most popular ones. Alkaline electrolyzers have been used for some decades, and now PEM electrolyzers are earning its fair share of attention.

I. PEM ELECTROLYZER

Even though there are some commercial models available, PEM electrolyzers have been developed for only about two decades. An electrolyzer of this nature typically operates below 80°C, using pressures as high as 100 bar, with a current density ranging from 0.5 to 2 A/cm². It can also handle very low part loads without difficulty. The main drawback of this kind of electrolyzers today is its cost, since the catalysts they use are noble-metal based [16].

PEM electrolyzers (the cell stack itself) mainly use metallic components and platinum or platinum alloys as a catalyst; the membrane is polymer-based. The anode, membrane and cathode are assembled in this order in a “sandwich fashion”. The electrolyzer system also needs a water supply and a pump, a power supply, water-gas separators and tanks, electronics for safety and control, and a heat exchanger [17]. It may also need an AC/DC converter depending on the electric source.

The most sensitive part to recycle in a PEM electrolyzer is the membrane. It can be recycled in a process that involves treating it with a lower alkyl alcohol solvent; this way the membrane (polymer) can be separated from the anode and cathode layers (noble metal). The obtained solution is then heated mildly so the polymer will be dispersed into particles. The polymer particles can then be separated from the noble metals by

¹**Heating value:** Quantity of heat released during the combustion of a certain amount of a substance. The *lower heating value* of a fuel is the amount of heat released by the combustion of a quantity of substance initially at 25°C and until the combustion products reach the 150°C back, which assumes the latent heat of vaporization of water in the combustion products is not being recovered. The *higher heating value* of a fuel, on the other hand, is the amount of heat released by the combustion of a certain quantity of substance at 25°C until the products of combustion return to 25°C, which takes into account the latent heat of vaporization of water in the reaction products [140].

filtration means. This recycling process is patented by BASF, and thus its details are not open to the public [18].

As for platinum resources, a book published by the U.S. Geological Survey (USGS, U.S. Department of Interior) in 2017, which focus on the analysis of the resources available for the mineral elements considered of vital importance for the United States' economy, states that there are enough reserves to meet the demands of platinum for many decades. It also comments on the disruptions of the platinum-group elements, which would be more likely to be linked with social, environmental, political, and economic factors than to resource depletion or geologic issues [19] [20]. These conclusions are corroborated by a more recent paper, stating that the most critical aspects about platinum resources are its social and environmental issues, and certainly not its net resource amount [21].

From the power-to-gas approach, a Proton Exchange Membrane (PEM) electrolyzer (7-8kW, depending on operation mode; commercial model) performance has been analyzed on different electrical sources setups in the University of California – Irvine. A first approach was done in 2017 to integrate photovoltaic power with the electrolyzer [22], and there is currently more research going on regarding other energy sources in this same institution.

II. ALKALINE ELECTROLYZER

Alkaline electrolyzers have been available in the market for some decades. Devices for operation up to a pressure of 30 bar and modules up to 2.5 MW are commercially available. They typically operate at around 80°C, with low current densities (0.2-0.4 A/cm²) [16], at a cell voltage of 1.8-2.2 V. Very high hydrogen purities are achieved (>99.8%). The theoretical maximum efficiency of electrolyzers is about 85%; under real conditions of operation, this number decreases to 65-75% (based on the lower heating value) [15 pág. 292]. Typical sizes of a cell block range from 1 to 800 Nm³/h, even though most electrolyzers sold today to laboratories and the semiconductor industry have a capacity of less than 60 Nm³/h. The electrolyte, in this case, is an aqueous potassium hydroxide (KOH) solution, usually from 20% to 40% KOH [15 pág. 291]. Hydroxide ions (OH⁻) are conducted in the solution. The electrodes are steel-based, the catalysts mainly nickel, cobalt or iron. The main drawback of the performance of alkaline electrolyzers in a power-to-gas approach is that their minimal part-load capability is limited by the gas conductivity of the diaphragm: in these cases, a fraction of the cell stack should not be used, so there must be a control system that operates all the stack or just a part of it depending on the load that needs to be met. Even though the cell efficiency is similar in both alkaline and PEM electrolyzers, stack efficiency is higher in alkaline electrolyzers because PEM stacks tend to be smaller. On the other hand, alkaline electrolyzers are slower than PEM electrolyzers [16].

The cell of an alkaline electrolyzer is composed by the electrolyte solution where two electrodes are submerged. They are separated by a diaphragm, which should have a low electrical resistance [15 pág. 292]. This diaphragm is nowadays usually made of composite materials based on microporous polymers or ceramics. Examples of materials for this application would be polyphenylene sulfide (Ryton®) and polysulfone bonded ZrO₂ (Zirfon®). Even though platinum is considered to be the best catalyst for alkaline electrolysis, it is not used due to its high costs. That is why electrodes are usually made, instead, of nickel with added sulfur to the coatings in order to activate them (a structure known as Raney nickel). The most commonly used electrolyte in this case is, as said before, potassium hydroxide. The conductivity of the solution depends then

on the concentration of the solution and the temperature of operation, and will need to be optimized for each cell model [23].

Even though their basic functional procedure is the same, alkaline electrolyzers are usually differentiated by the pressure they use to work. In this regard, atmospheric pressure electrolyzers (1 bar absolute) and pressurized electrolyzers (10-30 bar) can be found. The main advantage of the pressurized electrolyzers versus the atmospheric technique is that since hydrogen is produced at a higher pressure, less compression is needed for its storage or distribution in pipelines. The drawback is that the purity of the product gets affected, for the gas permeability of the diaphragm is increased at higher pressures and temperatures [15 pág. 292].

At the end of the lifecycle of the device, the components need to be disposed of. The potassium hydroxide solution ought to be treated as hazardous waste and sent to an approved waste treatment facility, following federal and local regulations [24]. The recycling of composite materials is currently a drawback of this technology. Even though these kinds of materials are becoming widely used in a large range of industries, their heterogenic nature makes them extremely difficult to recycle. Recycling techniques are being developed, but the final products are of a relatively low quality and the processing costs are high. Consequently, the acceptance of these recycled products in the market is lacking [25]. Apart from that, studies show that the electrochemical performance of the electrodes decreases over time, due to both the deterioration of the electrode material and the formation of nickel oxides on its surface [26].

III. HIGH TEMPERATURE ELECTROLYZER

In the early 20th century Nernst developed the high-temperature electrolyte yttria-stabilized zirconia (YSZ, ZrO_2 doped with 15% Y_2O_3), which is used as the basis for solid oxide electrolysis (SOEC – high temperature electrolyzer or HTE: these electrolyzers operate typically at 900-950°C, even though their range goes from 800°C to 1000°C) and solid oxide fuel cells (SOFC). Even though the technology was invented long ago, it is still under development. The two technologies discussed before are considered low temperature electrolyzers (LTE) and they can reach efficiencies of about 75%, but their energy consumption is its main drawback. In this regard, HTE looks more attractive because the electrolysis of water is increasingly endothermic with increasing temperature, and the required electrical power is reduced at higher temperatures due to the Joule heating effect [27]. Furthermore, high-temperature residual heat from other processes could also be used [15 pág. 293].

The most common electrolyte used in SOEC and SOFC is ZrO_2 doped with 8mol% Y_2O_3 , because of

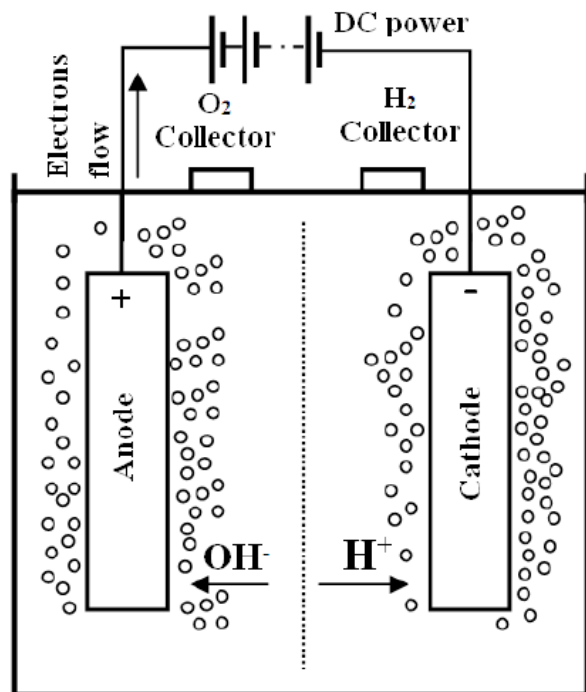


Figure 2. Basic scheme of a water electrolyzer.

Image extracted from https://www.researchgate.net/profile/Ahmed_Azmy5/publication/283504861/figure/fig1/AS:294315831771139@1447181770526/Basic-scheme-of-water-electrolysis-system.png [Accessed 02/18/18]

its high ionic conductivity and high thermal and chemical stability. The cathode is usually made of porous cermet composed of YSZ and metallic nickel, while the most common material used in the anode is a composite of YSZ and strontium doped lanthanum manganite (LSM), which is also porous [28].

The design of these cells has been traditionally planar, consisting basically of series of interconnected cell stacks. Alternative designs are being considered. Back in

1985, Dönitz and Erdle published a paper describing a high-temperature electrolyzer that featured a tubular shape. They claimed to have operated single cells during long-term tests with current densities of 0.3 A/cm^2 and 100% Faraday efficiency at a voltage of 1.07 V. The tubes were built connecting in series cylindrical cells of 1.0 cm long and 1.4 cm in diameter. A diagram of the tube can be observed in Figure 3 [29]. Even though planar designs are cheaper, they are more difficult to pressurize due to being more prone to mechanical fractures [30]; that is why the tubular design has been utilized for further research at various institutions. Researchers from Toshiba have more recently continued to work on the subject and they have been collecting data of the process in order to be able to create a model and to write a simulator. They are developing a HTE plant coupling with a nuclear reactor [31]. Another approach was taken by Martinez-Frias et al., who used this cell geometry to create a high-efficiency, solid-oxide natural gas-assisted steam electrolyzer, its differentiating feature being that while in conventional systems most of the electric power is used in forcing the oxygen to diffuse through the electrolyzer against a chemical potential, this novel approach used natural gas to react with the oxygen product (the reaction being either total or partial oxidation). By doing so, the chemical potential across the electrolyzer was reduced and, as a result, the electricity consumption was also reduced by 1 V in single cells, comparing to regular electrolyzer consumption. When this new design is equipped with a heat recovery system consisting of heat exchangers and a catalytic reactor, a high-efficiency (up to 90% based on total energy input) hydrogen production system is obtained. Efficiency increases as the fraction of methane utilization increases, and as the current density decreases [30].

1.3.2. Hydrogen as an energy source

Hydrogen is known for having a really high energy content. This energy is released in the strongly exothermic reaction that takes place when it combines with oxygen (O_2) to form the highly stable and low

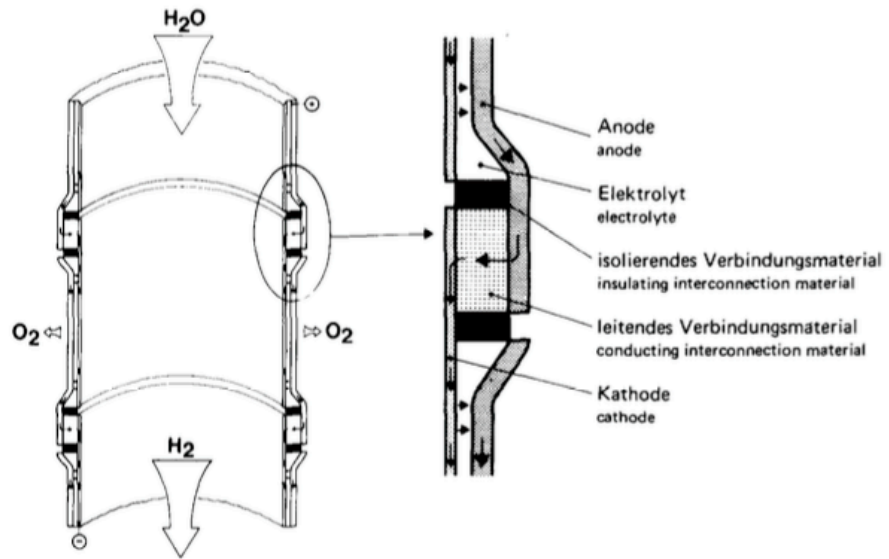


Figure 3. Illustrative diagram of the cell unit in a tubular electrolyzer. Extracted from *High-temperature electrolysis of water vapor - Status of development and perspectives for application*. Dönitz, W. and Erdle, E. 5, 1985, International Journal of Hydrogen Energy, Vol. 10, págs. 291-295.

energetic compound: water. On the basis of the respective combustion reaction, hydrogen has nearly three times the energy content of gasoline (120 MJ/kg for hydrogen; 44 MJ/kg for gasoline). As it can be seen in the Figure 4, hydrogen has an energy content vastly superior to all the fuels it has been compared to, if considering energy to weight ratio. When considering energy content to volume ratio, however, the situation is reversed, and hydrogen has only about a quarter of the energy content of gasoline (8.5 MJ/L for hydrogen and 32.6 MJ/L for gasoline, respectively). This is the main reason why hydrogen storage is regarded as challenging. Since hydrogen is, in normal conditions, a lightweight gas, research in storage strategies which focus on increasing energy density is needed [15].

I. POSSIBLE PATHWAYS

Hydrogen, as a fuel, can be utilized in a variety of ways. The power-to-gas approach is usually coupled with the eventual utilization of hydrogen to produce electricity again, but other pathways can be taken:

Electrolysis for grid support. In this case, an electrolyzer would provide ancillary services² to grid operators, doing frequency control and ramping services. Electrolysis units are built on purpose for wholesale energy services, unlike traditional demand response services [11].

Integration of large-scale, central renewables. Wind and solar energies are, by nature, highly variable. When the electricity they produce is not being utilized, it can be converted to hydrogen, which can be stored, injected into a natural gas transmission pipeline or delivered by other means, or reconverted to grid electricity [11]. However, it is always preferable to use the energy created by renewable sources directly to avoid the energy losses that come from the conversion to hydrogen and the reversion back to grid electricity. For example, in the hypothetical case that the yield from photovoltaics (PV) was about 337,500 kWh per ha and year, if PV electricity was converted to liquid hydrogen (LH₂), stored, and then converted back to electricity by a combined cycle gas turbine (efficiency 57.5%), about 104,000 kWh of electricity would be generated per ha and year. This yield would be more than three times the yield of the best biomass pathway: biogas via large gas engine, which could yield at most 33,500 kWh per ha and year with an efficiency of 46% for the engine [15 pág. 248].

Reconversion to grid electricity. This option is displayed as viable mainly for remote locations, the drawback of it is that is economically challenging in grid-connected systems, the reason being that too much energy is lost in both the conversion processes, and thus the efficiency of the process suffers is notably lowered. The reconversion, when done, can be performed either by fuel cells or turbines (thermal conversion units). The oxygen obtained as a byproduct of electrolysis can be utilized to increase combustion or fuel cell efficiencies. This option may be feasible in regional power networks that require long-term energy storage and where natural gas networks, gas storage and gas turbine power plants already exist.

² **Ancillary services:** “Those services necessary to support the transmission of electric power from seller to purchaser, given the obligations of control areas and transmitting utilities within those control areas, to maintain reliable operations of the interconnected transmission system. Ancillary services supplied with generation include load following, reactive power-voltage regulation, system protective services, loss compensation service, system control, load dispatch services, and energy imbalance services” [144].

Part 1: Worldwide energy demand and renewable resources

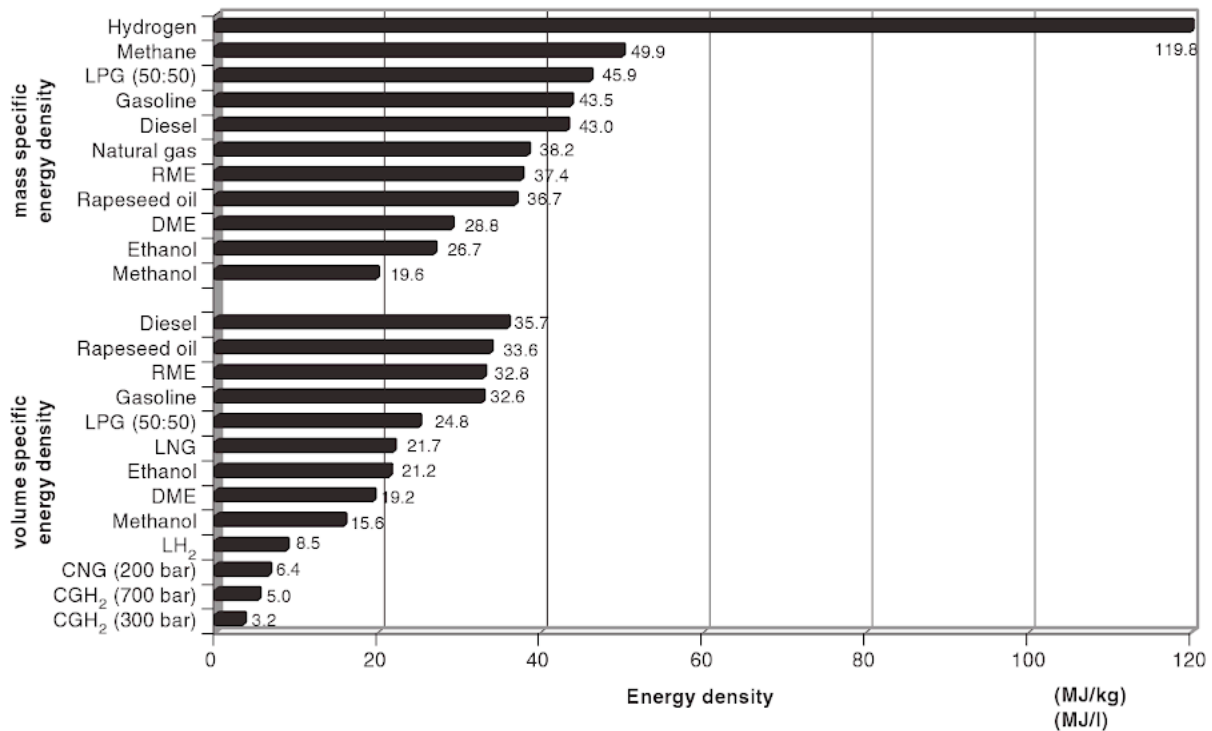


Figure 4. Energy densities of various fuels. In the graph, LPG stands for a mixture of propane and butane in the given ratios. Natural gas is 83% methane. Figure extracted from Ball, M. y Wietschel, M., [ed.]. The Hydrogen Economy: Opportunities and Challenges. New York : Cambridge University Press, 2009. p. 275. ISBN: 978-0-521-88216-3.

Distributed production from variable sources. Hydrogen can be produced large scale or small scale, closer to the point of end use. The electricity that is not used right away can be sent to the distribution grid or to electrolysis units. If the last option is chosen, the hydrogen that has been produced can be stored, used on-site or injected into natural gas distribution pipelines. The advantage of using distributed electrolyzers over a centralized system is that the flexibility for grid support is increased.

Methanation for renewable gas synthesis. Methane can be synthesized using hydrogen through the thermocatalytic process of methanation. In this process, carbon dioxide (CO₂) and hydrogen (H₂) are converted to methane (CH₄). Carbon monoxide (CO) can be also used instead of CO₂. If the hydrogen used has been produced using renewable sources, the methane that is obtained as a product can be regarded as a renewable gas [11].

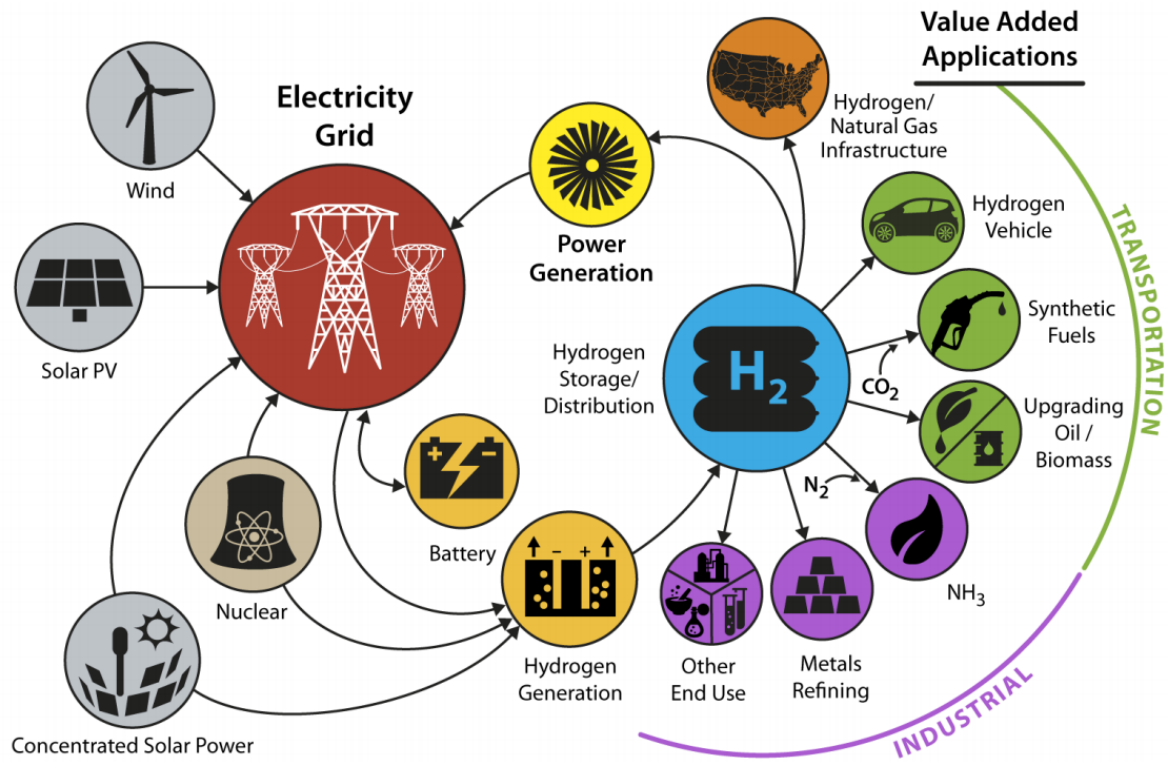


Figure 5. Hydrogen applications and production pathways. Image extracted from <https://www.nrel.gov/docs/fy16osti/66246.pdf> [Accessed 08/05/18]

II. SAFETY

For more than a century, hydrogen has been produced and used for commercial and industrial purposes –chemical processes in refineries and rocket propulsion among them–, which means that it has been handled only by well-trained personnel. If hydrogen becomes available for the population to use as an everyday energy carrier, people with no background on its safety will be handling it: safety regulations and technology will be needed so as to avoid accidents.

Since it has been utilized as a fuel in the past, hydrogen has taken part in a number of accidents. The causes of these episodes are varied: mechanical or material failure, corrosion attack, overpressurization, enhanced embrittlement of storage tanks at low temperatures, boiling liquid expanding vapor explosion, rupture due to impact by shock waves and missiles from adjacent explosions, human error... An example of one of these accidents would be the Hindenburg Disaster, which occurred in New Jersey in 1937, and which involved the ignition of the hydrogen gas used for buoyancy of the airship Hindenburg. The tail of the craft caught on fire, which provoked an explosion. The airship crashed onto the ground and 36 people were killed [32].

This signified the end of the zeppelin era, but it was certainly not the beginning. The first German airship made its initial flight on 1900. Zeppelins were used in World War I, and they even did flights of almost 100 hours of duration. Later on they were used for transatlantic flight service. The Graf Zeppelin started its operation in 1928 and by the time of its decommissioning had made 590 flights, 144 of which were ocean

crossings, and had flown more than one million miles. The Hindenburg had already made several trips, but after the accident, the fabrication of the airships was never resumed [33].

Another example of a hydrogen disaster would be the explosion –equivalent to 2.4 t of TNT– that took place in a polyethylene plant in Pasadena, Houston, in 1989, as a result of the release of a process gas during maintenance on a reaction loop line. Numerous defects in the management of the installation were detected in the investigation after the explosion: lack of a hazard assessment study, inadequate safety distances between the control room and the reactor, lack on an effective permit system for maintenance activities, and erroneous design of building ventilation, among others. 22 people lost their lives and 100 were injured. The plant was also extensively damaged [32].

III. HYDROGEN PROPERTIES ASSOCIATED WITH HAZARDS

In Figure 6 some thermophysical, chemical and combustion properties of hydrogen can be observed, as well as the respective value for the more widely known and utilized fuels gasoline and methane (methane is also considered to be a promising gaseous fuel for engine applications). The *limiting oxygen index* is the minimum concentration of oxygen that will support flame propagation in a mixture of fuel vapors and air. In the case of hydrogen, No flame propagation is observed at normal temperature and pressure (NTP) conditions if the mixture contains less than 5 %vol of oxygen. *Burning velocity* in NTP air for hydrogen depends on mixture composition, temperature, and pressure.

Hydrogen gas is colorless and odorless, which means that humans cannot detect it by themselves, no matter how high the concentration of it. It is about 14 times lighter than air in normal conditions (this condition is also called buoyancy, and is the reason why hydrogen was utilized in zeppelins). Since it's lighter than air, it moves upward and the ignition hazards are reduced because of that. The burning velocity of hydrogen can be relatively high, which means that confining or arresting hydrogen flames can be notoriously complicated, and explosion confinement is much more difficult to achieve in detonations where velocities are three orders of magnitude faster.

Liquefied hydrogen (LH₂) can cause frostbite burns or hypothermia if splashed onto the skin or into the eyes. The fact that the vents and valves in storage vessels may be blocked by accumulation of ice also needs to be taken into account. Ice may form because of the moisture in the air. If that happens, pressure can build up and the situation may result in mechanical failure with jet release of hydrogen and probably in a boiling liquid expanding vapor explosion. It is recommended that storage vessels are kept under positive pressure to prevent air from entering and producing flammable mixtures. These considerations need to be taken into account in addition to the ones that one would take when dealing with hydrogen gas [32 pág. 539]. Standard storage systems are designed considering heat leaks –hydrogen stored will eventually warm to ambient temperature, which means that the pressure will rise, so some hydrogen will be let out–, usually equivalent of 0.5% per day of the liquid contents [32 págs. 539-541].

IV. PHYSIOLOGICAL, PHYSICAL AND CHEMICAL HAZARDS

Hydrogen dangers need to be known and considered if this gas is going to become a fuel that is widely available. Its hazards can be classified in physical –concerning mainly embrittlement and deterioration of mechanical properties of the materials hydrogen is in contact with–, chemical –flammability, ignition sources,

and explosion phenomena–, and physiological –human-suffered consequences after an accident with hydrogen.

Physical hazards

- **Hydrogen embrittlement.** Degradation of the mechanical properties of the materials of the containment systems. It can result in leaks. Hydrogen embrittlement depends on many factors, the following among them: environmental temperature and pressure, purity of metal, concentration and exposure time to hydrogen, stress state, physical and mechanical properties, microstructure, surface conditions, and the nature of the crack front of the material [34].

Property	Value		
	Hydrogen	Methane	Gasoline
Heat of combustion (low) (kJ/g)	119.93	50.02	44.50
	119.70	46.72	44.79
Heat of combustion (high) (kJ/g)	141.86	55.53	48.00
	141.70	52.68	48.29
Flammability limits in NTP air (vol%)	4.0–75.0	5.3–15.0	1.0–7.6
			1.2–6.0
Flammability limits in NTP oxygen (vol%)	4.1–94.0	—	—
Detonability limits in NTP air (vol%)	18.3–59.0	6.3–13.5	1.1–3.3
	13.5–70.0		
Detonability limits in NTP oxygen (vol%)	15–90	—	—
Stoichiometric composition in air (vol%)	29.53	9.48	1.76
Minimum ignition energy in air (mJ)	0.017	0.29	0.24
	0.02	0.28	0.25
	0.14		0.024
Autoignition temperature (K)	858	813	501–744
			500–750
Adiabatic flame temperature in air (K)	2318	2148	~2470
		2190	
Thermal energy radiated from flame to surroundings (%)	17–25	23–33	30–42
Burning velocity in NTP air (cm/s)	265–325	37–45	37–43
Detonation velocity in NTP air (km/s)	1.48–2.15	1.39–1.64	1.40–1.70
Energy of stoichiometric mixture in NTP air (MJ/m ³)	3.58	3.58	3.91
Diffusion coefficient in NTP air (cm ² /s)	0.61	0.16	0.05
Buoyant velocity in NTP air (m/s)	1.2–9.0	0.8–6.0	Nonbuoyant
Limiting oxygen index (vol%)	5.0	12.1	11.6
Maximum experimental safe gap in NTP air (cm)	0.008	0.12	0.07
Quenching gap in NTP air (cm)	0.064	0.203	0.200
Detonation induction distance in NTP air	L/D ~100	—	—

Figure 6. Selected Comparative Properties of hydrogen, methane, and gasoline. NTP (Normal Temperature and Pressure): 293.15 K (20°C), 101.3 kPa.

Sources: After NASA, *Safety Standard for Hydrogen and Hydrogen Systems*, Report NSS 1740.16, 1997, chap.2; Adamson, K. A. and Pearson, P., *J. Of Power Sources* 86, 548, 2000; Karim, A., *Int. J.Of Hydrogen Energy*, 28, 569, 2003; Hord, J., *Int. J.Of Hydrogen Energy*, 3, 157, 1978; Baker, W.E. and Tang, M.J., *Gas, Dust and Hybrid Explosions*, Elsevier, Amsterdam, 1991; Rosyid, A. and Hauptmanns, U., *System Analysis Safety Assessment of Hydrogen Cycle for Energetic Utilization*, *Proc. Int. Cong. Hydrogen Energy and Exhibition*, Istanbul, 2005.

Extracted from: Gupta, Ram B., [ed.]. *Hydrogen Fuel. Production, transport and storage*. Boca Raton : CRC Press. Taylor & Francis Group, 2009. Págs. 540. ISBN: 978-1-4200-4575-8

Embrittlement can be environmental (surface cracking), internal (absorption) and caused by chemical reactions between the absorbed hydrogen and one or more of the compounds present in the metal [35]. Studies have shown that a metal or alloy is more susceptible to experiment deterioration of mechanical properties the stronger it is. It also generally increases with tensile stress [36] [37] [38].

- **Low-temperature mechanical properties of structural materials.** The mechanical properties of great interest for hydrogen applications at low temperature are transition from ductile-to-brittle behavior, certain unconventional modes of plastic deformation, and mechanical and elastic properties changes due to phase transformations in the crystalline structure [32 pág. 542]. Different materials have different thermal contraction coefficients, which need to be taken into account for safety reasons when designing a system designated to operate at cryogenic temperatures [34].

Chemical hazards

A number of safety measures are taken in installations handling hydrogen; these include the elimination of all likely sources of ignition. An investigation of industrial accidents in the United States for the period 1968-1977 showed that 53% of them occurred due to leaks, off-gassing, and equipment ruptures [39].

- **Flammability of hydrogen.** The flammability limits of mixtures of hydrogen with air, oxygen, or other oxidizers depend on the ignition energy, temperature, pressure, presence of diluents, and size and configuration of the equipment, facility, or apparatus. Mixtures of liquid hydrogen and liquid or solid oxygen are not hypergolic, but the ignition energy is very small and they can detonate when initiated by a shock wave [40]. *Diluents and halocarbon inhibitors* can be added to hydrogen mixtures to reduce the flammable range. Measurements performed for the water vapor at 422K (149°C) have shown that water is the most effective diluent [41] [42]. Other diluents are CO₂, N₂, He and Ar. The *autoignition temperature* of hydrogen in air is similar to the one of hydrogen in oxygen. This temperature depends on hydrogen concentration, pressure, and surface of containers. The *quenching gap* –or quenching distance–, is the dimension of the gap needed to prevent the propagation of an open flame through a flammable fuel-air mixture that fills the passage. In parallel-plate configurations, the quenching gap is defined as the spark gap between two flat electrodes at which ignition of combustible fuel-air mixtures is suppressed—it depends on the temperature, pressure, and composition of the combustible gas mixture and the electrode configuration. The three major factors that determine the quenching distance for gaseous fuels are ignition energy, mixture composition, and pressure [40] [32 págs. 544-545].
- **Ignition sources.** Potential ignition sources ranked according to frequency of occurrence are: open flames, hot works, electrical (short circuits, sparks, arcs), hot surfaces, personnel smoking, friction, spontaneous ignition, autoignition, hot particles, static discharge, and others [43]. The *minimum spark energy for ignition* is defined as the minimum spark energy required to ignite the most easily ignitable concentration of fuel in air and oxygen. The ignition energy for hydrogen, methane and gasoline is relatively low, which means that ignition in air is quite certain in the presence of any weak ignition source (sparks or matches, among others). *Hot objects and flames* can ignite hydrogen mixtures with air or oxygen. Objects at temperatures from 500 to 581°C can ignite mixtures at

atmospheric pressure. Objects at 317°C can ignite them after prolonged contact at less than atmospheric pressure [32 págs. 545-546].

- **Explosion phenomena.** A rapid energy release and pressure rise that can occur in both reactive and nonreactive systems is referred to as an explosion. In gas explosions, it is frequent to find the transmission of a wave, be it a deflagration wave –the flame front moves through a flammable mixture in the form of a subsonic wave with respect to the unburned mixture– or detonation wave – the flame front coupled to a shock wave propagates through a detonable mixture in the form of a supersonic wave with respect to the unburned mixture–. Gaseous mixtures explosions are classified into *unconfined vapor cloud explosions* (UVCE) or *confined vapor cloud explosions*(CVCE). A *flash fire* is a phenomenon that happens in a mixture within flammability limits: the flame front travels in the cloud at low velocity and insignificant pressure increase. In the case of liquid hydrogen, a *boiling liquid expanding vapor explosion* (BLEVE) can occur if a sudden release of a large mass of pressurized liquid is released into the atmosphere [32 págs. 546-547].

Physiological hazards

Safety measures need to be taken by personnel that are present during leaks, fires or explosions of hydrogen mixtures with air. Possible hazards for such people may be the following:

- **Asphyxiation.** Can occur when oxygen concentration is lowered below 19.5 vol%, a situation which can happen in a region where a leak of hydrogen or another nontoxic gas has happened.
- **Overpressure injury.** Result of the blast waves, consequence of an explosion.
- **Thermal burns.** Caused by the radiant heat emitted by a hydrogen fire. These burns are proportional to exposure time, burning rate, heat of combustion, size of the burning surface, and atmospheric conditions, mainly wind and humidity [32 pág. 541].
- **Cryogenic burns.** These may occur if a person is exposed to cold fluids (e.g. hydrogen spills) or cold vessel surfaces. If the zone of exposure is big, it could result in hypothermia [40].

1.4. Power-to-gas in the world

The historical usage (from 1950 to 2016) of renewable energy in the United States is represented in Figure 7. The chart shows how renewable energy usage increased in the 70s until the mid-80s (probably due to the oil crisis), then decreased, and in 2001 it started to gain popularity again, even though it did so at a slow pace. 2016 was the first year when its part in the total energy consumption was greater than 10%, albeit shyly. The reader can acknowledge the most relevant historical events surrounding the whole period below.

In the 50s, petroleum and natural gas became the most used fuels, petroleum because of the demand caused by the automobile, and natural gas due to its increasingly popular home usage, which could be possible thanks to the extensive construction of natural gas pipelines done throughout the 50s and 60s. In 1951 a nuclear reactor produced electricity for the first time, and the first commercial nuclear power plant begun operation in Pennsylvania in 1957. The Organization of Petroleum Exporting Countries (OPEC) was formed in 1960 in Bagdad by Iran, Iraq, Kuwait, Saudi Arabia and Venezuela. Other countries later joined:

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Qatar in 1961, Indonesia in 1962 (its membership was then suspended in 2009), Socialist Peoples Libyan Arab Jaahiriya (1962), United Arab Emirates (1967), Algeria (1969), Nigeria (1971), Ecuador (1973, suspended membership from December 1992 to October 2007), Angola (2007) and Gabon (1975-1994). In 1962, the first geothermal power plant was built in northern California. In early 1969, the Santa Barbara Oil Spill drew national attention to the environmental consequences of energy exploitation. 235,000 gallons of crude were leaked, thus creating a slick of 800 miles. In 1970, the U.S. government passed the Geothermal Steam Act in 1970 in order to allow the leasing of land containing geothermal resources to motivate geothermal energy development.

In 1973 the OPEC oil embargo caused gas shortages and rationing. This embargo was the response of the OPEC to the U.S. decision to re-supply the Israeli military during the Arab-Israeli War, and it affected both the U.S. and the rest of the countries that supported Israel. It banned petroleum exports and introduced cuts in oil production. Oil prices rose spectacularly, its consequences global. At the time, the dollar was also experiencing devaluation. A large oil fuel reserve in Alaska had been discovered in 1968. Immediately after the announcement of the Arab oil embargo, the Congress decided to construct a pipeline traversing Alaska to transport the oil. The Trans-Alaska Pipeline System (TAPS) was built because of the importance of minimizing the nation's dependence on foreign oil, even though many environmentalists protested the construction in the roots of the potentially destructive effects the pipeline could have. Starting in the mid-70s, NASA led an effort to develop and advance the technology and enable large commercial wind turbines. In late 1975, the Strategic Petroleum Reserve was formed and President Ford signed into Law the Energy Policy and Conservation Act, the purpose of which was to reduce the impact of severe energy supply interruptions.

In 1977, the Solar Energy Research Institute was formed by the U.S. Department of Energy. The attention was being dragged to alternative energy sources and how to use them so the dependency on gas and oil could decrease, as President Carter said in 1977. NASA put a good amount of efforts in developing PV technology. In 1979 an accident in one of the reactors in the nuclear plant in Pennsylvania planted a feeling of uneasiness in the population. The world's first wind farm was built in 1980 in New Hampshire; the first large-scale solar-thermal power plant begun operation in 1981. Also in this year more wind farms are being built, but environmentalists were starting to be concerned because a high number of birds were being killed because of them. In 1986, the Chernobyl nuclear accident took place in the former Soviet Union. In 1989, the largest oil spill in U.S. waters happened in Alaska: the Exxon Valdez disaster, with devastating consequences for the environment. In 1990, the Congress passed an Act to stimulate the development of hydrogen power. Hydrogen started to be thought about as a fuel to reduce dependence on conventional fuels, and the idea was to be able to widespread its use. Further Acts reinforced this idea in 1996 and 2003. In 1994, the U.S. begun importing more petroleum than it actually produced.

In 2007, the Intergovernmental Panel on Climate Change (IPCC) confirmed that the climate change was actually happening, mostly as a result of human activities. The National Biofuel Action Plan was unveiled in 2008 as another means to decreasing the dependency on fossil fuels. With the same objective, President Obama signed the American Recovery and Reinvestment Act in 2009, and funding for biofuels, solar and geothermal energies were also announced, as well as investments to modernize the energy grid. In 2010, another oil accident took place in the coast of Louisiana, becoming the largest oil spill in U.S. history. In 2011, the solar power company Solyndra declared bankruptcy after receiving more than \$500 million in federal loan guarantees. In 2012, the U.S. Nuclear Regulatory Commission (NRC) approved new nuclear

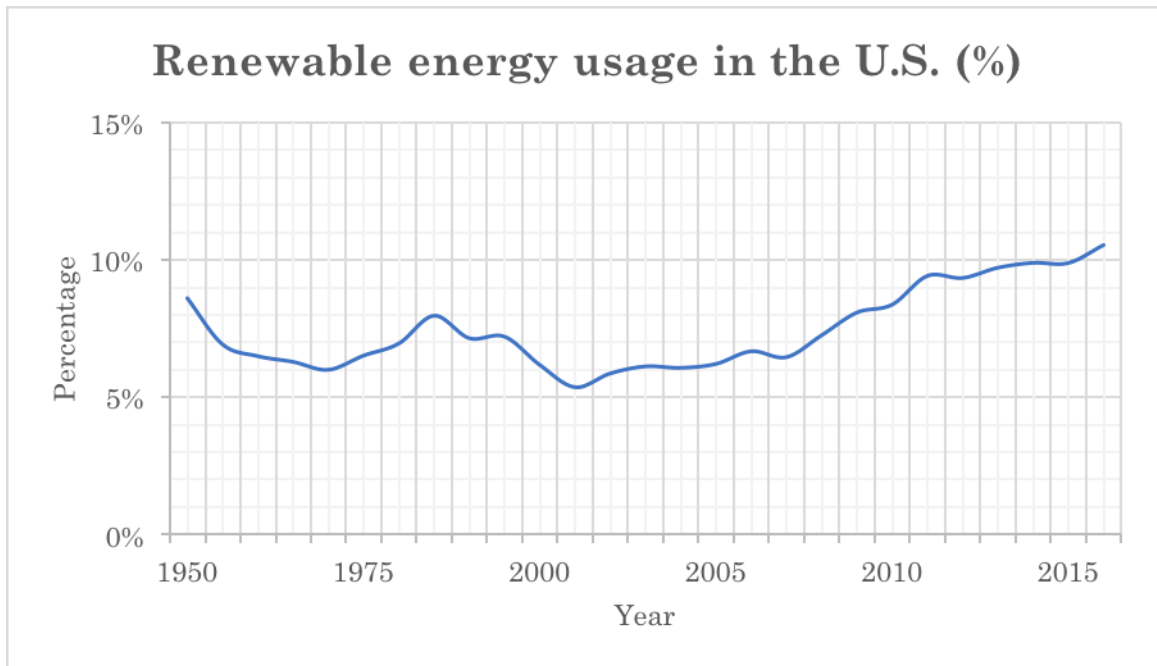


Figure 7. Renewable energy usage in the U.S. from 1950 to 2016. Data source: https://www.eia.gov/totalenergy/data/monthly/pdf/sec1_7.pdf [Accessed 03/21/18]

power plants for the first time since 1978, and the first Clean Air Act standard for carbon pollution from new power plants was also announced. President Obama released in 2013 his Climate Action Plan, which had the goal that the federal government would consume 20% of its electricity from renewable sources by 2020, among others. In 2014, Ivanpah, the World's largest concentrated solar power generation plant –with a capacity of 392 MW– went online. Further solar power commitments and executive actions were announced. Rockefellers and over 800 global investors announced fossil fuel divestment. In 2015 President Obama announced Clean Power Plan, which was reversed by President Trump in 2017 [44].

In Europe, the natural gas infrastructure is well developed, both on- and off-shore. The total capacity of offshore wind farms could reach a capacity of around 100 GW by the year 2030. The PV capacity is expected to increase to almost 60 GW in 2020. For example, power-to-gas technology is considered in Germany because of the necessity to transport the energy from the northern area, where the large wind potential is, to the southern area, where most of the industry is located and therefore a large amount of energy is needed. This transport could be achieved since there is an existing gas infrastructure with enough capacity between these two regions [45].

The consumption of energy per capita in the world has increased quite steadily over the years. The average MWh per capita (amount per year) can be observed in Figure 8. It is important to notice that the amount represented is the average, and the actual amount differs enormously between developed and non-developed countries. In 1971, the average amount was 1.36 MWh: at the highest end was Norway with 14.08 MWh, and at the lowest end was Nepal with $6.04 \cdot 10^{-3}$ MWh. In 2014, the average was 3.94 MWh: the largest amount per capita, 53.83 MWh, was consumed in Iceland, while the smallest amount, $38.97 \cdot 10^{-3}$ MWh, was consumed in Haiti [46]. Not all countries of the world were taken into account in these calculations –the information is not available for all countries–, but the majority of them were. The fact that the average is much closer to the lower end of the spectrum than the higher end implies that the number of countries that

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consume high amounts of energy per capita, which are highly developed, is much smaller than the ones that consume small amounts.

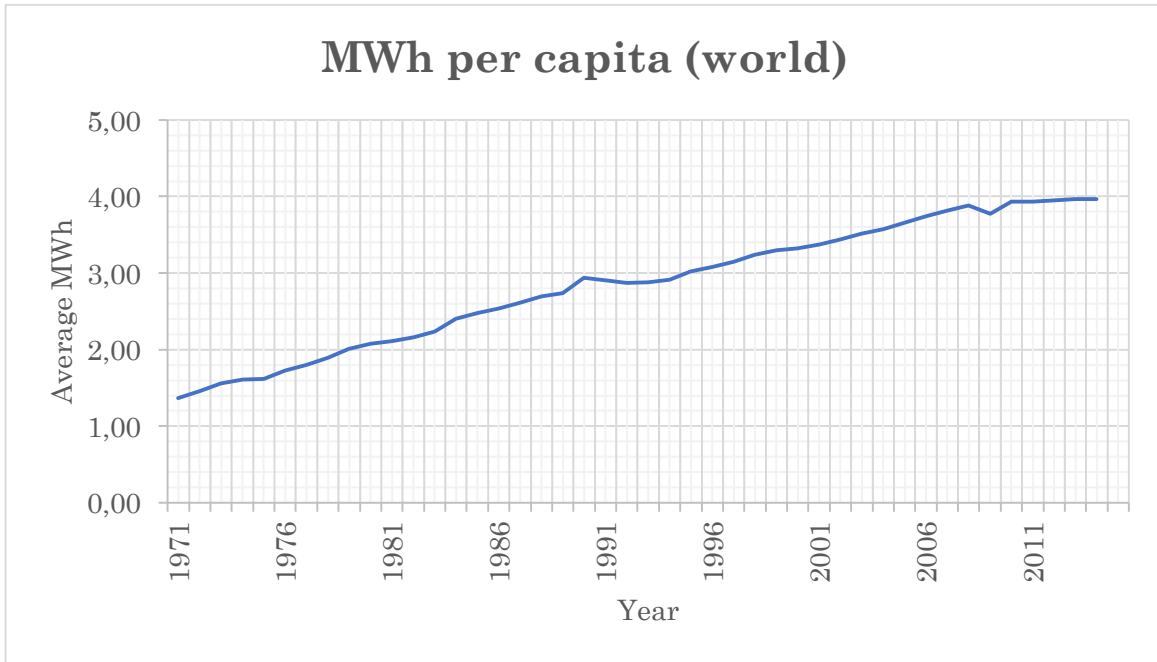


Figure 8. Average world MWh consumption per capita. Data source: <https://data.worldbank.org/indicator/EG.USE.ELEC.KH.PC> [accessed 03/21/18]

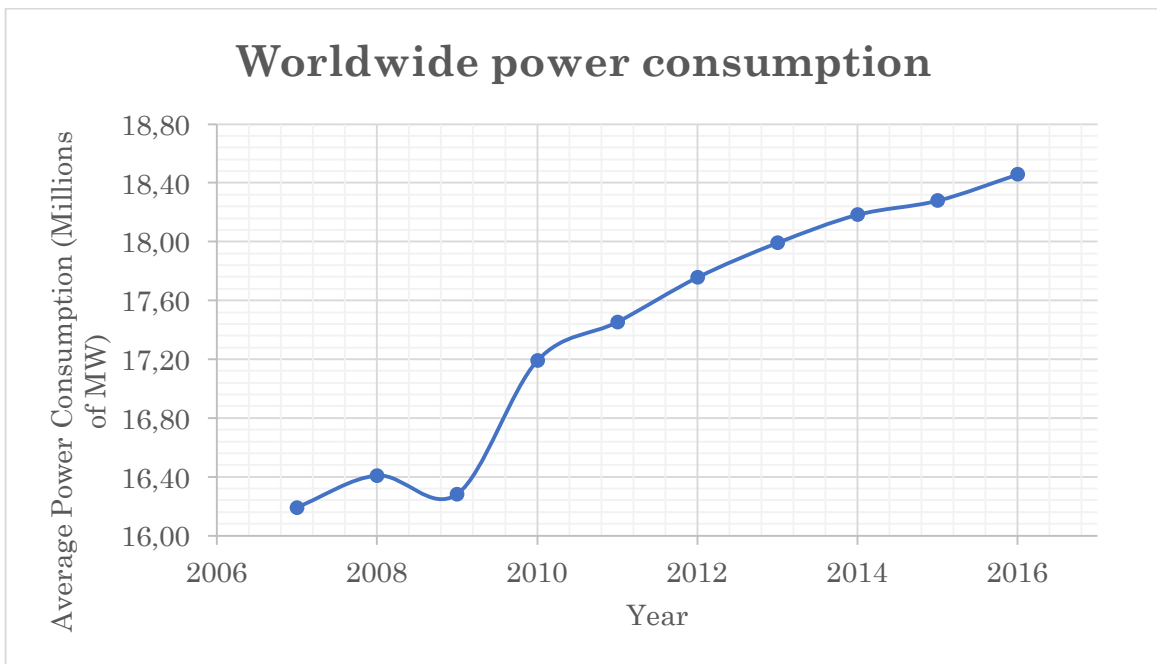


Figure 9. Worldwide power consumption from 2007 to 2016. Hourly average. Source: <https://yearbook.enerdata.net/total-energy/world-consumption-statistics.html> [Accessed: 03/21/18]

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The development of power consumption along the years can be observed in Figure 9. While MWh per capita seems to increase in a more or less steady pace, a minimum in 2009 can be observed by the naked eye, probably as the consequence of The Great Recession of 2008. In the data, not the totality of the countries of the world is considered, since the data about some countries is not available, even though it is for most of them. The represented power is the average consumed in one hour for the whole world. In 2007, 16,191,433.16 MWh were consumed in one hour in average in the totality of the world; in 2016, 18,457,787.3 MWh [47], which represents an increase of 14% in nine years.

The renewable capacity (Figure 10), on the other hand, has been increasing steadily worldwide along the years, but it is by far not enough to fuel the world utilizing only renewable sources. Also, the capacity must always be a little higher because it refers to the maximum power that could be produced but, since renewable sources are not always available, one cannot have a steady generation that equals the capacity value. In 2007, a capacity of 989,213 MW was available; in 2016 MW, 2,006,202 MW [48], an increase of 102.81%. Even though the increase is quite impressive for such a short period of time, it only went from representing 6.11% of the total averaged power consumed hourly in 2007 to 10.89% in 2016. These figures are obtained when doing the following calculation,

$$\text{Capacity vs. consumption ratio} = \frac{\text{renewable capacity}}{\text{average hourly power consumption}} \cdot 100 \quad (1)$$

and the development of the quotient along the years can be observed in Figure 11. Data about capacities was extracted from IRENA [48], and consumption from Enerdata [47]. A comparison chart between average hourly power consumption and capacity along the years is illustrated in Figure 12.

When looking at the consumption and capacity amounts in a continental level, some trends can be observed. First of all, it is important to take into account that the amounts calculated for this purpose and represented in Figure 13 and Figure 14 needed to be estimated because the two sets of data were not recorded in exactly the same way. These values are, therefore, and as previously stated, an estimate, which aims to illustrate the trends regarding consumption and renewable capacity development in each continent. They were calculated in the following manner:

Table 1. Detail about the calculations used to obtain the values for continental renewable capacity and consumption.

Capacity [48]		Consumption [47]	
<i>Estimated value</i>	<i>Calculation</i>	<i>Estimated value</i>	<i>Calculation</i>
Africa	Africa	Africa	Africa
America	North America + Central America + Caribbean + South America	America	America
Asia	Asia + Middle East + Eurasia / 2	Asia	Asia + Middle East + CIS / 2
Europe	Europe + Eurasia / 2	Europe	Europe + CIS / 2
Oceania	Oceania	Oceania	Oceania

As for power consumption in every continent, the amounts displayed in Figure 13 are again calculated as an hourly average. For the period 2007-2016, very little change is observed in most of the continents. The

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amounts remain quite stable over the years for Oceania, Africa, Europe and America, though the effects The Great Recession can be appreciated in 2009 for Europe, America and Asia. The continent that has notably increased its power consumption over this period is Asia, possibly because of the rapid development and the growing industry in China and India. Asia consumed in hourly average 7,010,641.42 MW in 2007, the figure rising to 9,231,329.24 MW in 2016 [47], which implies a 31.68% increase. Another continent that has increased its averaged hourly consumption is Africa, with a 24.81%. The rest of the continents experienced decreases in consumption in this period, in 0.55%, 5.81%, and 2.90% for America, Europe, and Oceania, respectively. The continent that consumes the most energy is Asia, followed by America, Europe, Africa and Oceania, in decreasing order.

The trends in installed renewable capacity follow different patterns, which are showed in Figure 14. In 2016, Asia was the continent with the highest renewable capacity installed, followed by Europe and America, which are in the same range, and by far by Africa and Oceania, also in a similar range. It is also interesting to compare the change of capacity to consumption ratio in the different continents from the beginning of the period studied, in 2007, to the last year from which data is available, 2016, which is done in Figure 15. The ratio increases in the period for all the continents, but with varying degrees. The highest ratio value in 2007 was Europe, with 8.91%, closely followed by Oceania, 8.82%, and America, 7.69%. These figures are increased for the year 2016. Europe continues to be the leading in the ratio value, with 17.30%, followed again by Oceania, 14.01%, and America, 12.18%. As for the increases in each continent for this period, increases of 8.39%, 5.19%, 4.93%, 4.50% and 0.90% are observed in Europe, Oceania, Asia, America, and Africa, respectively.

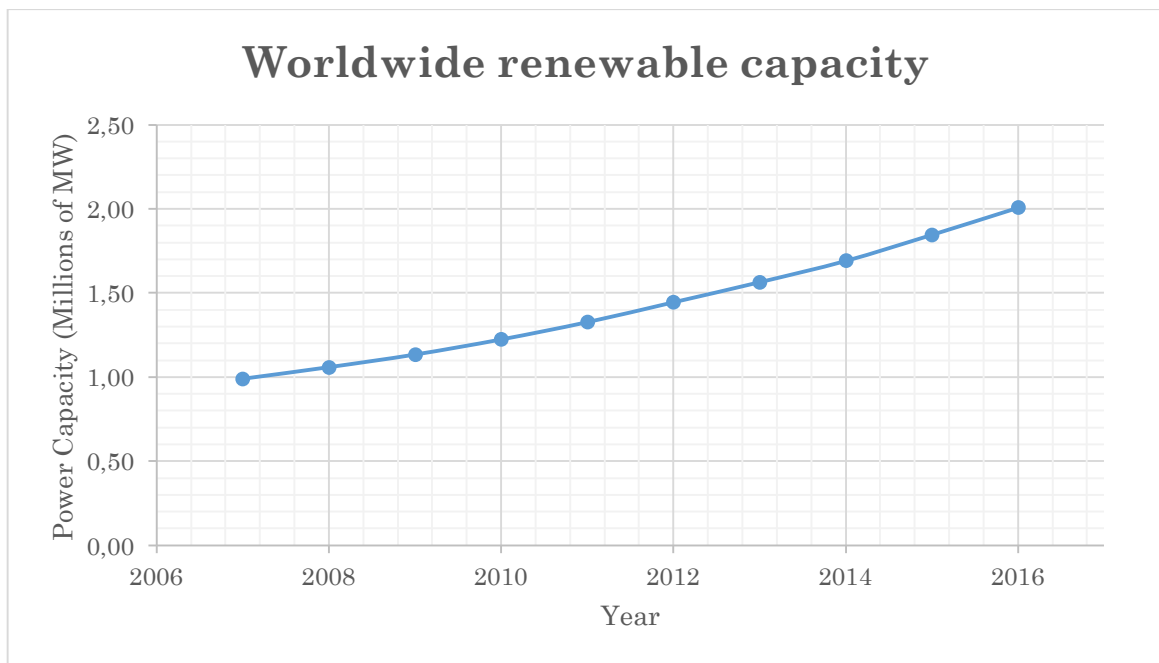


Figure 10. Worldwide renewable capacity from 2007 to 2016. Source:

<http://www.irena.org/publications/2017/Mar/Renewable-Capacity-Statistics-2017> [Accessed: 03/21/18]

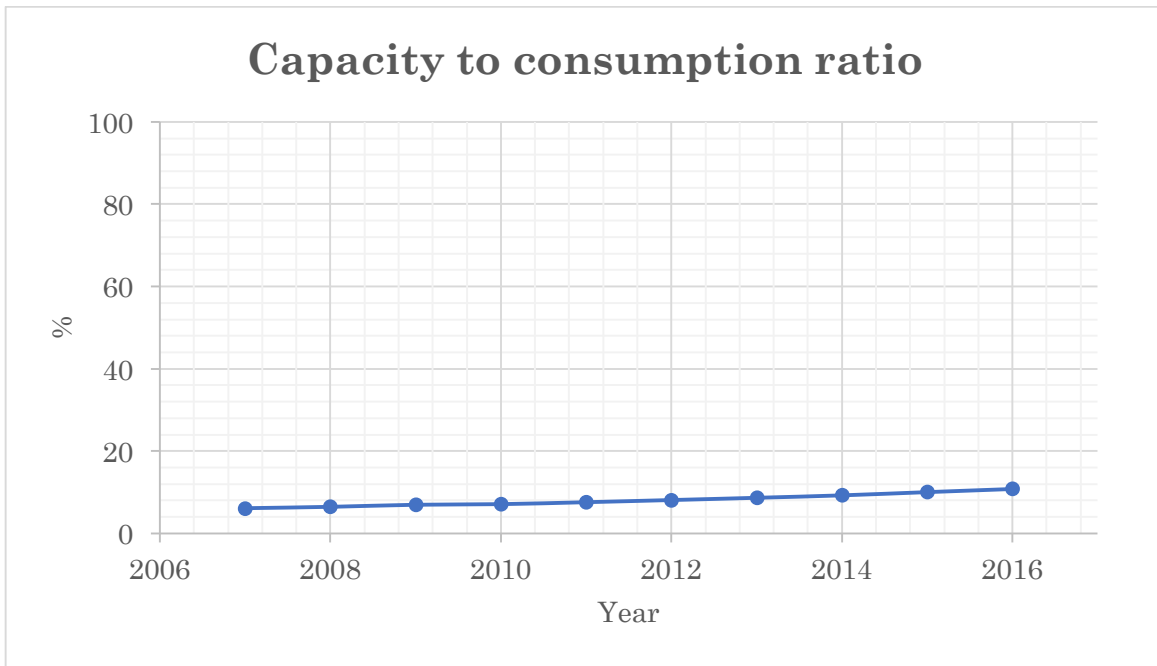


Figure 11. World capacity to consumption ratio from 2007 to 2016. The chart displays the results obtained when using equation (1). Lowest figure is 2006 with 6.11%, and highest in 2016 with 10.89%.

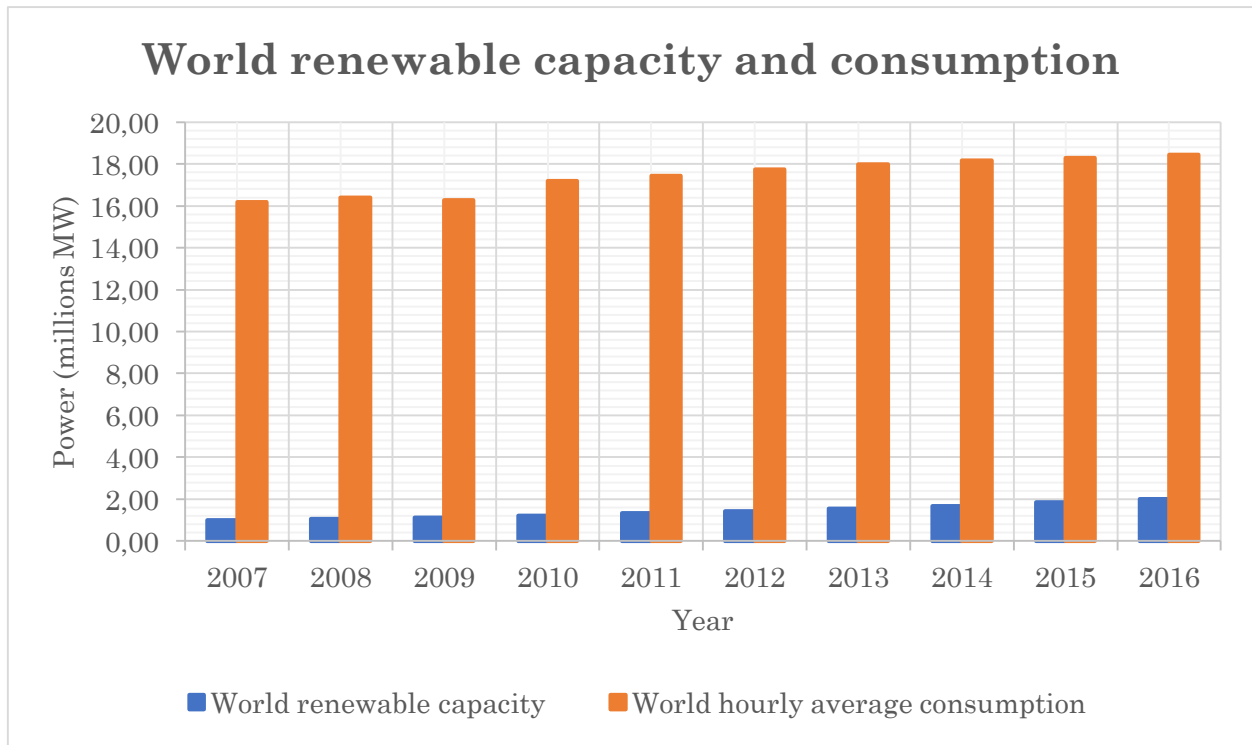


Figure 12. World renewable capacity and consumption. The chart compares the installed renewable capacity with the hourly average consumption.

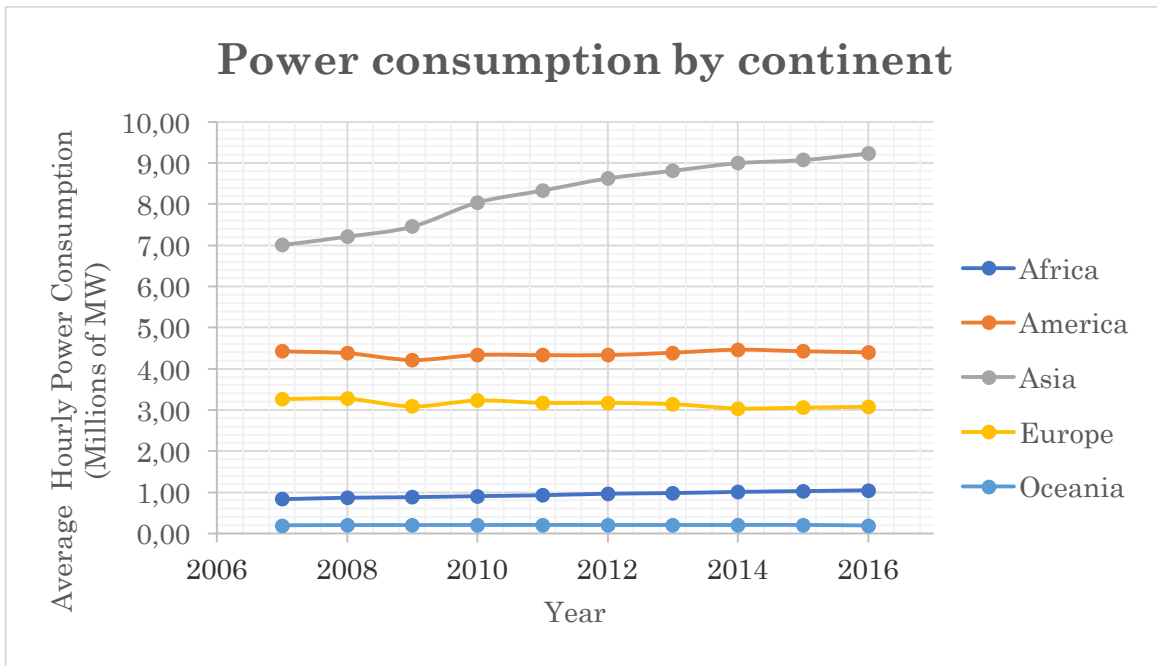


Figure 13. Average hourly power consumption by continent. Source: <https://yearbook.enerdata.net/total-energy/world-consumption-statistics.html> [Accessed: 03/21/18]

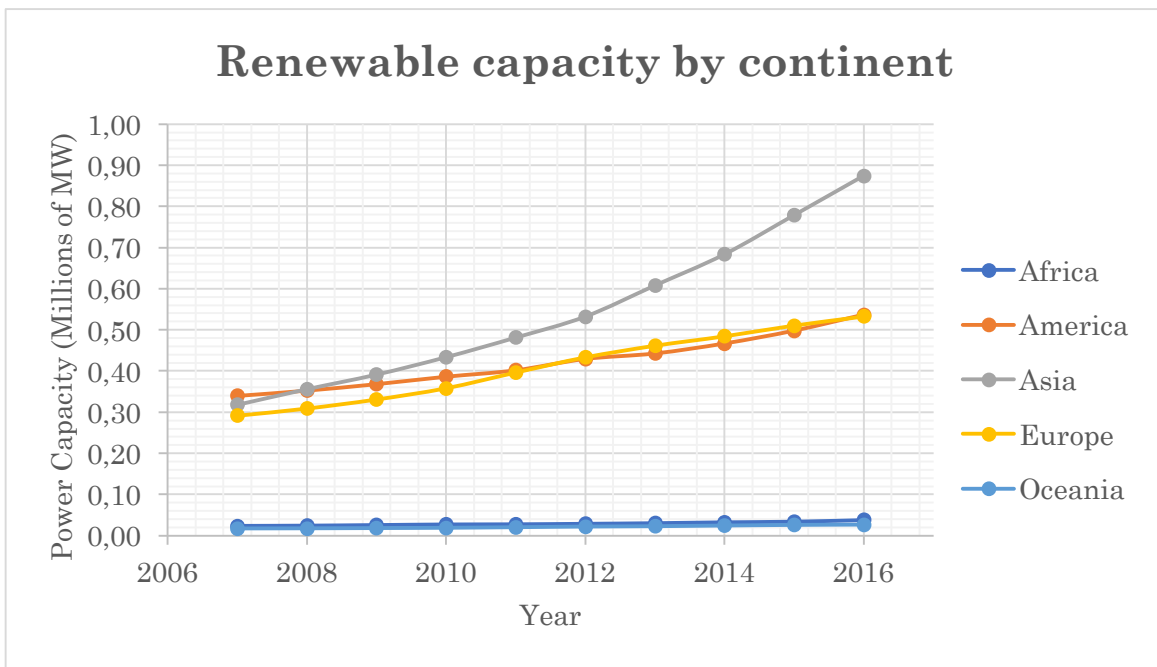


Figure 14. Renewable power capacity by continent. Source: <http://www.irena.org/publications/2017/Mar/Renewable-Capacity-Statistics-2017> [Accessed: 03/21/18]

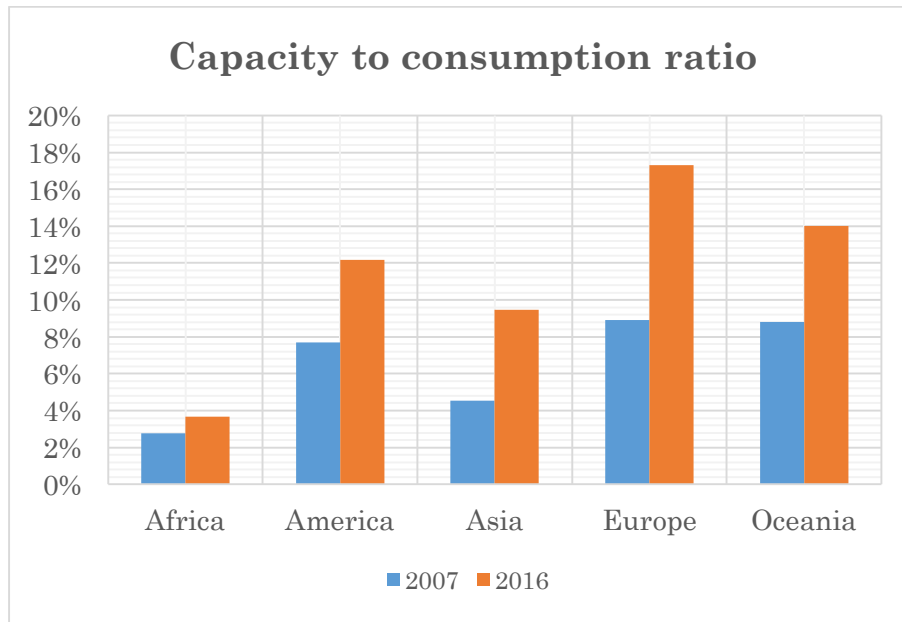


Figure 15. Capacity to consumption ratio per countries, 2007 to 2016 comparison.

1.5. Dynamic storage for a 100% renewable economy

1.5.1. Dynamic storage for power plants using electrolysis

McVay did in his dissertation an evaluation of dynamics reversible chemical energy storage with high temperature electrolysis: the goal was to calculate how much renewable energy capacity would be needed to be able to supply enough energy to the grid relying only on renewable sources and curtailing the energy they produced when it was not being fully utilized in existing natural gas storage facilities, which could be converted into hydrogen storage facilities. He found that, considering the renewable power capacity available in California and its actual storage facilities, a scaling factor of 11.16 would be needed for the renewable power to meet the demand. That would result in a renewable capacity of 89.2 GW. This scaling factor was then multiplied by another factor when the hydrogen storage profile was analyzed.

When doing the calculations, it is considered that the tank start being half filled. The optimal scaling factor had to fulfill the following criteria: (1) be able to store as much otherwise curtailed renewable power as hydrogen as possible, (2) hydrogen energy storage facilities should always be in use (avoid them being both completely empty or full), and (3) the fill level at the end of the year should be the same as the fill level at the beginning of the year.

After analyzing the data with various scaling factors, it was observed that, generally, the fill level of the tank went down during the winter months, and filled up during the summer months due to the increased PV output. When using the factors 1.4 to 2.0, the tank was filled up too quickly and it became incapable of storing otherwise curtailed energy, but the fill level at the end of the year was closer to the starting fill level. With factors 0.9 to 1.2, the tank experienced early depletion and low fill levels at the end of the year. Using factor 1.3, the tank was neither depleted nor fully filled, but the end-of-the-year level was found to be

relatively low. The most favorable scenario happened when using a factor of 1.34, which would mean that the renewable capacity would increase to 119.5 GW [49].

1.5.2. Renewable energy potential

Every region in the world has its own climatological characteristics and, as a consequence, some energy sources may be more plausible than others in a certain area. In this chapter, the renewable potential for a few areas will be discussed. It is important to note that only wind and PV energy will be considered for this purpose.

Fossil fuels share in the electricity mix is bound to decrease in the next couple decades, its main two reasons being the increasing prices due to both geological depletion and restriction of exported oil by the producing countries to gain political leverage, and the high greenhouse gases emissions, especially carbon dioxide, that they are responsible for. Nuclear power is not likely to substitute it as it has a high cost, the fact that a long time is needed in order to build a nuclear plant, and the widespread political opposition to it, based on the fear of accidents (e.g. Chernobyl in 1986, Fukushima in 2011) and the problems with its radioactive waste and reactor safety. This creates a context where renewable technologies are likely to increase its importance in the global energy production. The problems renewable energy will have to overcome are closely linked to climate change constraints. The technical potential for solar energy will vary with on-going climate change, and wind energy potential will fall if temperature differentials between equatorial and polar regions continue to fall [50].

I. DEFINITIONS

- **Geographical potential.** Energy flux theoretically expectable in areas that are considered suitable and available for energy production, what is to say, areas not excluded by other incompatible land use or constraints (e.g. minimum average wind speed, solar radiation regime).
- **Technical potential.** Derived from the geographical potential considering some assumptions on the development of conversion efficiencies [51].

II. SOLAR ENERGY

Even though there are a number of renewable energy sources available, solar is by far the most popular to install in households. Its demand has grown consistently by 20%-25% per year over the past 20 years, since its cost has gone down. Though its efficiencies are low, they are gradually increasing. Lower prices and higher efficiencies make them increasingly cost-effective, and thus more attractive to the market [52]. Sociological studies have also been made in order to determine what motivates the adoption of residential solar electricity. A particular study suggests that environmental values alone are not enough, and are not always necessary, to motivate adoption; and rational economic calculation in the sense of payback period is less important than the particular timing of economic events within a household. A characteristic identified as generally motivating adoption was an interest in technical innovation and enjoyment of the technical aspects of energy systems [53].

Hayn et al. underlined in their study the fact that even though households were responsible for 29% of total electricity demand in Europe, a good understanding of their consumption and load profiles was missing.

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They noted that load profiles differed on the grounds of household size, net income and employment status. They also studied the capabilities of some renewable systems to supply energy to a load, and found that a combination of photovoltaic panels and storage systems was what worked best. They studied different strategies that utilized diverse devices (heat pumps among others) and noted that these substantially increased load demand [54].

The Earth receives annually $1.5 \cdot 10^{12}$ GWh of energy from the Sun [55]. The annual energy consumption in 2016 was 161,690,216.75 GWh [47], which makes the energy received from the Sun almost 10,000 times greater than the amount that is actually consumed. The averaged energy over the whole Earth surface that is received is 340 W/m^2 ; about 30% of which is reflected back to space and 20% is absorbed by clouds, dust and greenhouse gases [55]. A solar radiation map can be observed in Figure 16.

The global solar radiation reaching the Earth's surface is the addition of the direct and diffuse radiations. The fraction that travels unimpeded through both space and the atmosphere and reaches the surface is known as direct radiation; the fraction that is scattered by molecules found in the atmosphere is referred to as diffuse radiation. Direct radiation causes shadows and diffuse radiation is responsible for skylight [56].

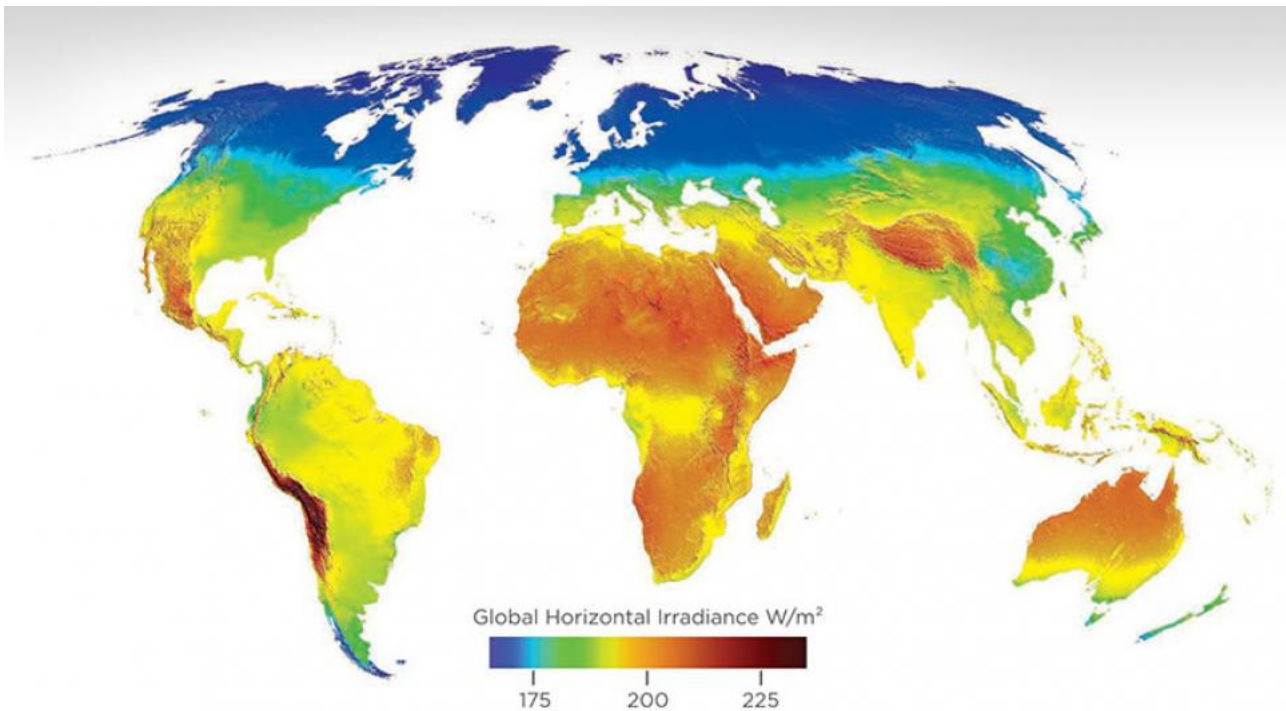


Figure 16. Solar irradiance world map. Source:

https://www.vaisala.com/sites/default/files/styles/16_9_liftup_extra_large/public/images/LIFT-Vaisala_global_solar_map.jpg?itok=XXM95zsr [April 18, 2018]

According to Hoogwijk's calculations, the global technical potential of grid-connected, both centralized and decentralized— PV was about 23 times the world electricity consumption of 2001. This figure is substantially reduced if plausible costs are considered. Regions that are considered high potential –1000 to 4000 times the electricity consumption– include north, east and west Africa and Australia. Japan, OECD

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Europe and Eastern Europe the potential is also higher but only two times the consumption, at the most. In a lot of areas the potential is affected by the lack of land in where to install a solar farm.

Solar-PV energy may be an economically viable option for future energy production, but its future depends largely on technological development, which is needed in order to keep the energy costs down. On the other hand, PV may be increasingly competitive in some small niche markets. The regions that are considered to have the best potential and to be economically viable for PV in 2050 are southern west USA, northern region and south of Africa, the Middle East, and Australia [51].

III. WIND ENERGY

Wind energy can be thought of as a consequence of solar radiation in the atmosphere. Sunlight falling on the ocean and continents causes air to warm and rise, which in turn generates surface winds. Wind energy is highly variable, affected by weather conditions and topography [55].

Hoogwijk studied in 2004 the global and regional wind potential. It is important to take into account that only onshore potential was considered due to lack of data on offshore wind power. It was stated that when comparing to the electricity consumption of 2001, the technical potential exceeded the electricity consumption in most regions, with the highest surplus found in East Africa –consumption level exceeded by more than 300 times–. In OECD Europe, it was about two times the electricity consumption, while in Eastern Europe it was less than the consumption. Half of the electricity consumption in Canada and the USA could be produced at reasonable costs by onshore wind farms.

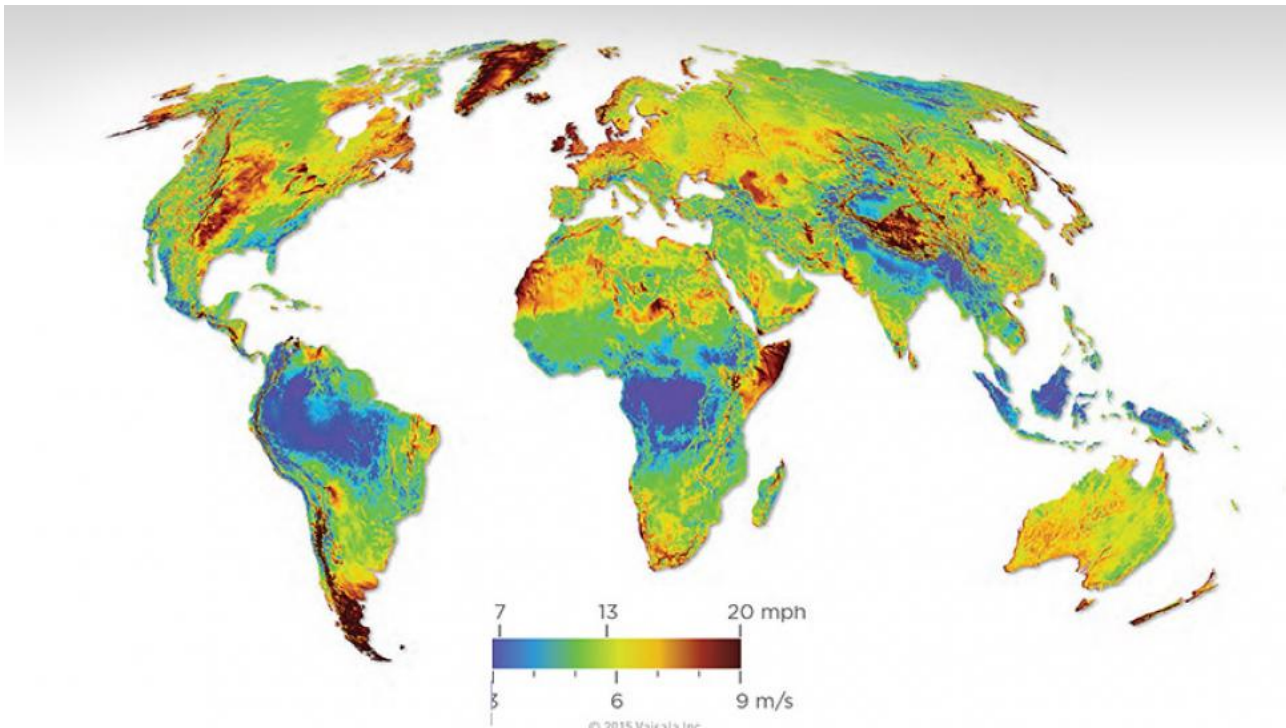


Figure 17. Wind potential world map. Source:

https://www.vaisala.com/sites/default/files/styles/16_9_liftup_extra_large/public/images/LIFT-Vaisala_global_wind_map.jpg?itok=Rgg8kins [April 18, 2018]

The author notes that the current situation of failure to absorb all wind or solar electricity produced has consequences in the electricity price of the electricity produced, making it more expensive. With about 20% of the energy supplied being from renewable resources, about 750 TWh and 500 TWh in the USA and in OECD Europe, respectively, are discarded yearly [57].

Wind power is found to be the most likely option to produce electricity at competitive prices, and its technical potential is higher than solar energy. The regions best suited for this energy in 2050 –considering both potential and economics– are center and north-west United States, north and west Canada, far south in South-America, northern Europe, eastern Europe, north of Russia, and northern region of Australia [51].

1.5.3. Factor and initial storage calculations

Data extracted from SMARD (Germany, Luxemburg, and Austria) and CAISO (California) from the year 2017 was used to calculate the estimated scaling factor that would be needed in order to produce enough power that, coupled with storage, could meet the energy grid demands, as

$$Factor \cdot renewable\ current\ generation\ profile \geq load\ demand \tag{2}$$

The capacity factor (CF) was calculated and used to identify which of the two renewable sources studied –wind and solar– was more productive in the area and so which one was the most interesting to invest in. The results obtained in the single-renewable-source scenario were also used as an indicator for this purpose. The one that needed the lesser scaling factor was favored.

Two scenarios concerning a different span of time are considered: firstly, some calculations are done in a 24-hour time-span. Two days picked at random are used for these calculations: an autumn day and a spring day. The autumn day is December 1st, 2017, and the spring day is June 1st, 2017. Afterwards, a calculation using a year worth (2017) of data is done.

I. CALCULATION METHODS

Scaling factors and approximate battery storage

Calculations were done using Mathwork®’s Matlab®. These calculations are only aimed at giving a rough idea of the daily battery storage that would be needed and daily surplus that would be obtained, and are in no case optimized.

The simplest scenario compares a single renewable profile with the load profile. The renewable-generated energy is less than the energy consumed. Therefore, a scaling factor (SF) that multiplies the renewable profile needs to be calculated. That is done by using a function that basically uses an iterative method to try a scaling

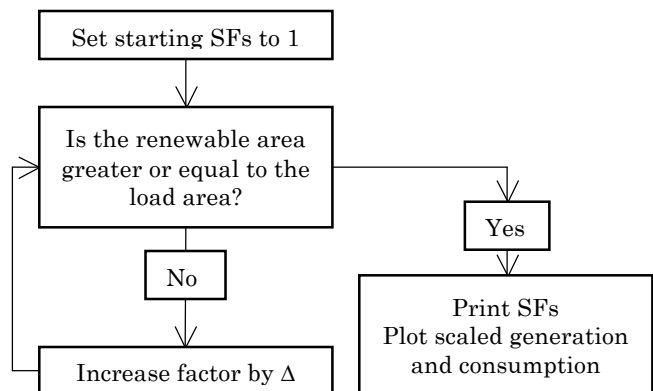


Figure 18. How the SFs are calculated.

factor and gradually increases it with a set delta (specifically $\Delta=0.01$) until the energy generated by the renewable source (renewable area) is equal or slightly greater than the energy consumed (load area). Then, storage is calculated by finding the intersections between the two curves –load and renewable generation–, and calculating the renewable area that is placed outside the load area. This is the amount of energy that will need to be stored in order to be available for the load when the renewable generation is not enough to supply the required energy.

The scenario that takes into account both wind and solar profiles is calculated in a slightly different way. In this case the algorithm only considers two types of renewables, but the method could be easily adapted to more profile inputs. Firstly, it is needed that the area formed by the wind area and the solar area are equal or greater than the load area. Again, this is done by using an iterative function that starts with scaling factors of 1 in both generation profiles and uses two different deltas to increase the scaling factors in each iteration. Different deltas were used for comparison, which will be showed in an example in the next section. To set the value for the deltas, the capacity factor was used as a mild indicator, along with the data

obtained in the calculations concerning only one renewable technology at a time. Whichever renewable had the higher capacity factor, would also be the one that had the larger delta, while the other renewable would remain at the base delta ($\Delta=0.01$). The conditions used are summarized in Table 2. The iteration stops when the sum of the renewable areas is equal or greater than the load area. To calculate the storage needed in this scenario, firstly each renewable is multiplied by its scaling factor, which has just been calculated, and then these profiles are summed. The summed profile is plotted along with the load profile and its intersections are calculated. Again, the renewable area that stands out of the load area will be the amount of storage needed.

For the calculations regarding the maximum power value, the knowledge of which is needed for the sizing of the electrolyzer, the following method is used: in each case, the load vector is subtracted from the scaled renewable profile –be it made of single or multiple renewable sources– and the maximum of the obtained vector is found. This is the maximum power value of the period studied.

Battery storage

The function that calculates the battery storage based on the data provided and a starting value for storage follows an iterative method that sets the starting battery state of charge at 50% of the initial storage given. It then adds the generation and subtracts the consumption for every value in the vector, and calculates the state of charge (SOC) in percentage. If at some point the state of charge of the battery is less than 0, then this element of the vector is set at 0; if it's more than 100, then this element of the vector is set at 100. When it reaches the final element of the vector, it evaluates it to see if it's inside a set interval (between 49 and 52% SOC). If it is, the resulting storage is printed and the SOC vector saved. If it is not, the storage is made 100 MWh bigger and the process starts again. SOC vector is plotted. The diagram for the described algorithm can be observed in Figure 6.

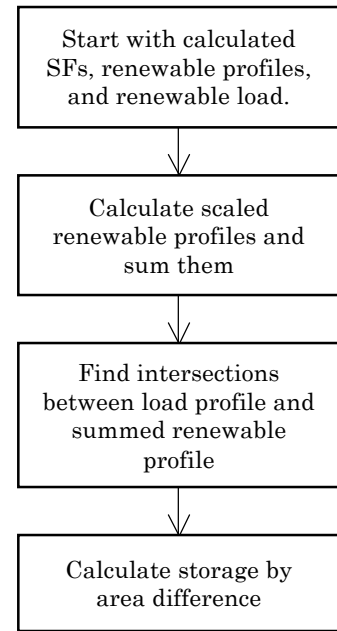


Figure 19. How the starting storage amount is calculated.

II. GERMANY, AUSTRIA AND LUXEMBURG REGION

24-hour results

In the Germany, Luxemburg and Austria region, solar was found to have a rather low capacity factor, 0.10, while wind had a factor of 0.24 [58]. The ratio wind CF / solar CF was then 2.4, indicating that in this area wind is a much more abundant and productive resource. Wind will therefore be the one favored to increase its scaling factor in the two-source scenario. The differences found between the autumn and the spring days are big, because solar irradiance is very low in the autumn day while there is a lot of wind, and in the spring day the productivity of wind is scarce and the sun shines much more than in the autumn day.

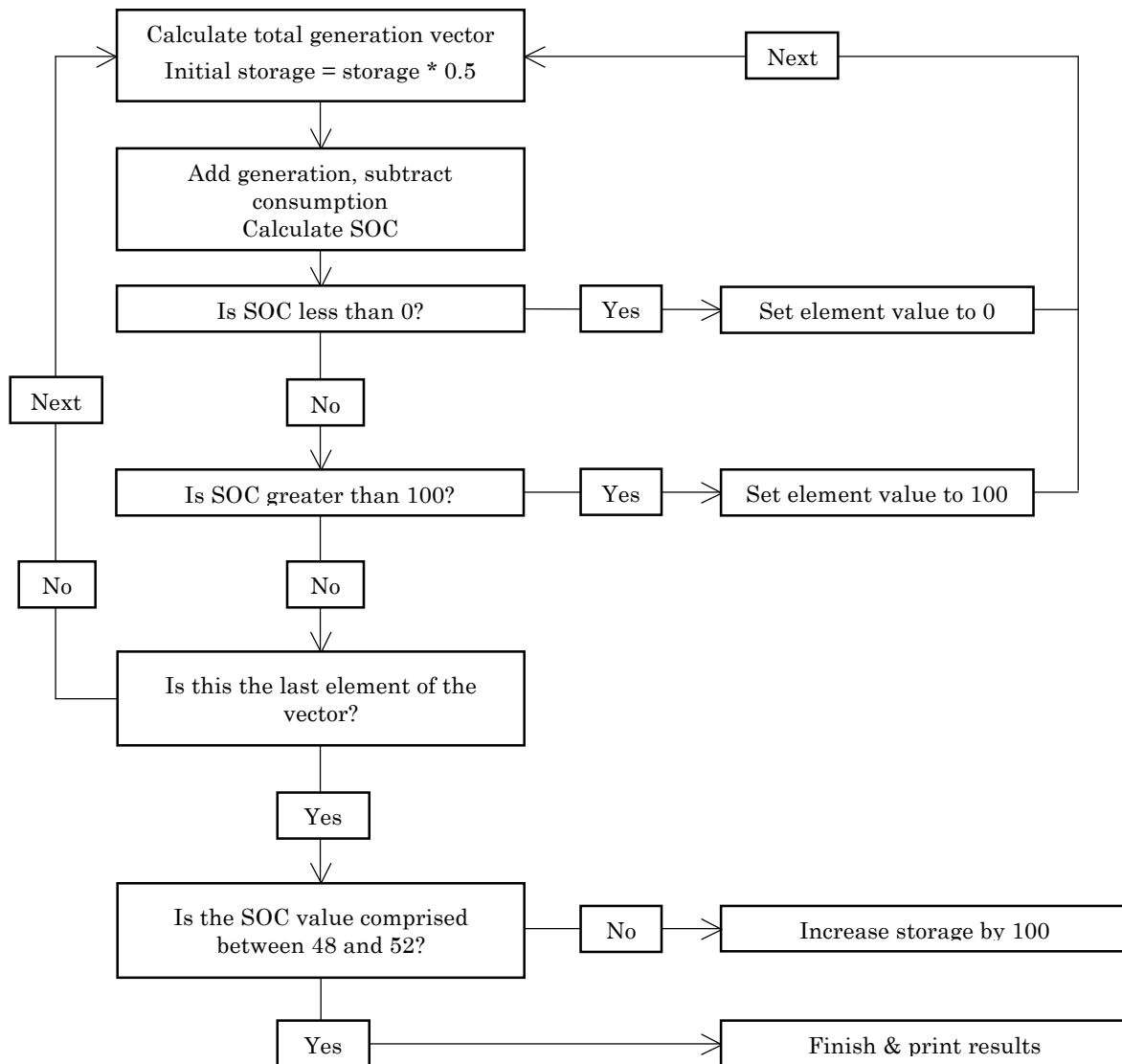


Figure 20. Algorithm for storage calculations.

Autumn day: when calculating the scaling factor using only one of the two renewable streams, it was calculated that a storage of 3,282,700 MWh for solar, with a scaling factor of 32.61 and a surplus of 1350.40

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MWh, and a storage of 508,740 MWh for wind, a factor of 3.84 and a surplus of 12,269MWh, respectively, were needed.

In the two-source scenario, the starting SF for both sources was 1. Delta for solar was in all cases 0.01, and different deltas for wind were tested. The results are listed in Table 3. The biggest storage necessity appears when using $\Delta_{\text{solar}}=\Delta_{\text{wind}}=0.01$. Both SFs will be 3.43 in this case, with a storage of 536,790 MWh. The smallest storage is found with the combination $\Delta_{\text{solar}}=0.01$ and $\Delta_{\text{wind}}=0.1$. SF for solar and wind in this scenario are, respectively, 1.27 and 3.7, the storage being of 489,040 MWh.

Regarding the sizing of the electrolyzer that would be needed, the solar energy only scenario is by far the one that needs the biggest electrolyzer, with 218,500 MW. In the two-renewable scenario results vary, but not much. All the results are listed in Table 3, as said previously. The scenario that would need the smallest electrolyzer is found when using $\Delta_{\text{solar}}=0.01$ and $\Delta_{\text{wind}}=0.02$, and it has a value of 14,279 MW.

Spring day: in this case, when calculating the scaling factor using only one of the two renewable streams, it was calculated that a storage of 2,665,000 MWh for solar, with a scaling factor of 6.76 and a surplus of 1,309.70 MWh, and a storage of 1,349,700 MWh for wind, a factor of 15.27 and a surplus of 1,747.30 MWh, respectively, were required.

In the two-source scenario, the biggest storage necessity appears when using $\Delta_{\text{solar}}=\Delta_{\text{wind}}=0.01$. Both SFs will be 4.69 in this case, with a storage of 1,646,300 MWh. The smallest storage is found with the combination $\Delta_{\text{solar}}=0.01$ and $\Delta_{\text{wind}}=0.1$. SF for solar and wind in this scenario are, respectively, 1.98 and 10.8, the storage being of 920,810 MWh.

Regarding the sizing of the electrolyzer that would be needed, the solar energy only scenario is by far the one that needs the biggest electrolyzer, with 101,070 MW. In the two-renewable scenario results vary from 28,951 MW (solar SF=2.66, wind SF=9.30) to 64,358 MW (solar SF=wind SF=4.69). All the results are listed in Table 3, as said previously.

Year results

Following the same calculation methods that were used in the day-to-day approach, results using a full year of data were obtained. The results differ from the day data calculations and they are more similar to the autumn day calculations than the spring day ones. This is to be expected since the area that is being studied is not an especially sunny one. The results are listed in Table 4.

In this case, the smallest storage scenario was found when using $\Delta_{\text{solar}}=\Delta_{\text{wind}}=0.01$, with SF=3.84, WF=3.84 and a storage of 540,270,000 MWh. The largest storage scenario was found when using $\Delta_{\text{solar}}=0.01$ and $\Delta_{\text{wind}}=0.1$, with SF=1.37, WF=1.37, and a storage of 592,600,000 MWh. The storage and electrolyzer results coincide: Lowest power is found with $\Delta_{\text{solar}}=\Delta_{\text{wind}}=0.01$, 123,490 MW, and highest power is found with $\Delta_{\text{solar}}=0.01$ and $\Delta_{\text{wind}}=0.1$, 132,960 MW.

III. CALIFORNIA REGION

24-hour results

In the California region, solar PV was found to have a CF of 0.34, while wind had a CF of 0.28. That means the solar CF per wind CF ratio is 1.21 [59] [60], which makes solar more desirable in this area. Even though California (especially southern California) is regarded as a sunny region, there is a rather large difference in the productivity of solar energy in an autumn and a spring day.

Autumn day: as it was done in the Germany, Luxemburg and Austria region, several combinations of deltas were tried for the two-renewable scenario. The largest storage appears when using $\Delta_{\text{solar}}=0.04$ and $\Delta_{\text{wind}}=0.01$, as a result a solar SF of 11.28 and a wind SF of 3.57 are obtained, with a storage of 4,303,080 MWh. The smallest storage necessity is found when using $\Delta_{\text{solar}}=\Delta_{\text{wind}}=0.01$ and SF for both solar and wind of 10.21, and it has a value of 3,841,080 MWh.

In the case of the electrolyzer, it is again the solar-only scenario the one that needs the biggest one, with 60,218 MW, but in this case this value is not that far from the maximum MW needed in the two-renewable scenario, mainly because in this case solar energy was favored. The values obtained in the two-renewable scenario do not hold a big variability. In the scenario of the solar SF of 10.90 and wind SF of 5.95, the electrolyzer needed should have a capacity of 55,027 MW. The scenario that would need the smallest electrolyzer would be the wind-only, with a capacity of 22,498 MW.

Spring day: in this case, when calculating the scaling factor using only one of the two renewable streams, it was calculated that a storage of 3,434,300 MWh for solar, with a scaling factor of 6.44 and a surplus of 8,588.60 MWh, and a storage of 1,171,100 MWh for wind, a factor of 8.25 and a surplus of 1,329.50 MWh, respectively, were required.

In the two-source scenario, the biggest storage necessity appears when using $\Delta_{\text{solar}}=0.04$ and $\Delta_{\text{wind}}=0.01$. In this case, solar SF is 4.92 and wind SF is 1.98, and a storage of 2,368,700 MWh is required. The smallest storage is found with the combination $\Delta_{\text{solar}}=\Delta_{\text{wind}}=0.01$. SF for solar and wind in this scenario are 3.62, the storage 1,441,500 MWh.

Regarding the sizing of the electrolyzer that would be needed, the solar energy only scenario is again by far the one that needs the biggest electrolyzer, with 34,664 MW. In the two-renewable scenario results vary from 13,621 MW (solar SF=wind SF=3.62) to 22,920 MW (solar SF=4.92, wind SF=1.98).

Year results

The difference in the calculated scaling factors is, in this case, greater than in the Germany, Austria and Luxemburg area.

The smallest storage was found when using $\Delta_{\text{solar}}=\Delta_{\text{wind}}=0.01$, with SF=5.88, WF=5.88, and a storage of 914,270,000 MWh. The largest storage scenario was found when using $\Delta_{\text{solar}}=0.04$ and $\Delta_{\text{wind}}=0.01$, with SF=7.68, WF=2.67, and a storage of 1,240,600,000 MWh. The storage and electrolyzer results again coincide: lowest power is found with $\Delta_{\text{solar}}=\Delta_{\text{wind}}=0.01$, 56,196 MW, and highest power is found with $\Delta_{\text{solar}}=0.04$ and $\Delta_{\text{wind}}=0.01$, 58,213 MW.

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The storage values calculated here are just the value of the renewable area not covered by the load area. They are going to be adjusted in next sections, and their value is going to be remarkably lower.

Table 2. Conditions used in each of the calculated scenarios

		Conditions			
		Solar		Wind	
		<i>Initial factor</i>	Δ	<i>Initial factor</i>	Δ
Germany, Luxemburg and Austria	#01a	1	0.01	-	-
	#02a	-	-	1	0.01
	#11a	1	0.01	1	0.01
	#12a	1	0.01	1	0.02
	#13a	1	0.01	1	0.03
	#14a	1	0.01	1	0.05
	#15a	1	0.01	1	0.1
	California	#01b	1	0.01	-
#02b		-	-	1	0.01
#11b		1	0.01	1	0.005
#12b		1	0.02	1	0.01
#13b		1	0.03	1	0.01
#14b		1	0.04	1	0.01
#15b		1	0.05	1	0.01

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Table 3. Results for the calculations of factors for solar energy and wind energy, daily battery storage necessities, daily battery surplus power, and maximum delta energy for the electrolyzer in each and every calculated scenario.

		Day-based results					
		Scaling factors		Battery		Electrolyzer	
		<i>Solar</i>	<i>Wind</i>	<i>Storage (MWh)</i>	<i>Surplus (MWh)</i>	$\Delta P \text{ max (MW)}$	
Germany, Luxembourg and Austria	#01a	32.61	-	3,282,700	1,350.40	218,500	AUTUMN DAY
	#02a	-	3.84	508,740	12,269.00	18,443	
	#11a	3.43	3.43	536,790	3,605.20	19,399	
	#12a	2.29	3.58	515,250	23,405.00	14,279	
	#13a	1.88	3.64	513,170	37,984.00	15,240	
	#14a	1.54	3.7	521,780	62,697.00	16,201	
	#15a	1.27	3.7	489,040	23,611.00	16,201	
	#01a	6.76	-	2,665,000	1,309.70	101,070	SPRING DAY
	#02a	-	15.27	1,349,700	1,747.30	74,922	
	#11a	4.69	4.69	1,646,300	7,178.30	64,358	
	#12a	3.82	6.64	1,225,000	1,055.70	48,848	
	#13a	3.29	7.78	1,072,400	14,403.00	39,556	
	#14a	2.66	9.30	986,820	17,248.00	28,951	
	#15a	1.98	10.80	920,810	2,664.00	37,231	
	California	#01b	11.83	-	4,536,360	789.02	60,218
#02b		-	74.61	989,124	97.37	22,498	
#11b		10.89	5.945	4,133,400	2,352.50	54,954	
#12b		10.21	10.21	3,841,080	1.36	51,136	
#13b		10.90	5.95	4,139,520	9,003.80	55,027	
#14b		11.14	4.38	4,241,040	3,511.40	56,358	
#15b		11.28	3.57	4,303,080	127,776.00	57,162	
#01b		6.44	-	3,434,300	8,588.60	34,664	SPRING DAY
#02b		-	8.25	1,171,100	1,329.50	14,894	
#11b		4.35	2.675	1,954,800	4,067.40	18,699	
#12b		3.62	3.62	1,441,500	12,0883.00	13,621	
#13b		4.36	2.68	1,967,300	20,102.00	18,804	
#14b		4.72	2.24	2,228,400	39,564.00	21,468	
#15b		4.92	1.98	2,368,700	36,380.00	22,920	

Table 4. Results for the calculations of factors for solar energy and wind energy, yearly battery storage necessities, yearly battery surplus power, and maximum delta energy for the electrolyzer in each and every calculated scenario.

		Year-based results					YEAR-BASED RESULTS
		Scaling factors		Battery		Electrolyzer	
		<i>Solar</i>	<i>Wind</i>	<i>Storage (MWh)</i>	<i>Surplus (MWh)</i>	$\Delta P \text{ max (MW)}$	
Germany, Luxemburg and Austria	#01a	15.16	-	1,317,400,000	805,620	371,500	
	#02a	-	5.14	662,580,000	4,278,900	150,820	
	#11a	3.84	3.84	540,290,000	4,253,400	123,490	
	#12a	2.63	4.26	545,490,000	8,794,900	123,550	
	#13a	2.14	4.42	555,590,000	6,224,300	124,790	
	#14a	1.72	4.6	582,640,000	22,770,000	130,040	
	#15a	1.37	4.7	592,600,000	14,983,000	132,960	
California	#01b	9.12	-	1,504,000,000	1,447,000	66,616	
	#02b	-	16.54	887,130,000	764,070	56,443	
	#11b	6.93	3.965	1,099,700,000	146,480	57,157	
	#12b	5.88	5.88	914,270,000	1,866,400	56,196	
	#13b	6.94	3.97	1,102,800,000	4,027,600	57,270	
	#14b	7.39	3.13	1,183,600,000	55,873	57,595	
	#15b	7.68	2.67	1,240,600,000	1,138,000	58,213	

It is important to take into account that the battery storage calculations are concerning a 100% efficient battery, so no roundtrip efficiency has been considered. Therefore, in the event of putting the results presented here into practice, the characteristic roundtrip efficiency for the battery being used should be considered.

1.5.4. Variability

I. MONTH-BASED RESULTS

Monthly consumption and generation

The generation and consumption energy amounts were studied for the year 2017 in the California and Germany, Luxemburg and Austria region. In these calculations, only solar and wind energy are considered.

In **Germany, Luxemburg and Austria**, the renewably-produced energy accounts for between 18% and 48% of the energy consumed. The lowest ratio is observed in January, 18%, followed by a far 38% in February and November. The rest of the months are above 40%, with the highest, 48%, in October. The smallest amount of energy is produced in January; the biggest in October and December. The consumption varies along the year, but the variability is relatively less than in the California scenario. The results for this area are illustrated in Figure 21.

Part 1: Worldwide energy demand and renewable resources

For a seasonal shifting option it is of vital importance to study if there may be generated energy that is not being used during a period of time that could be saved for later use. In this region, the energy consumption is lowered during the time span comprised from April to September, and the months where the consumption is highest are November, December and January. On the other hand, the energy production from March to June is relatively high, so considering a scaled generation profile, it might be possible to save some energy in this period in order to use it in the highest-consumption months.

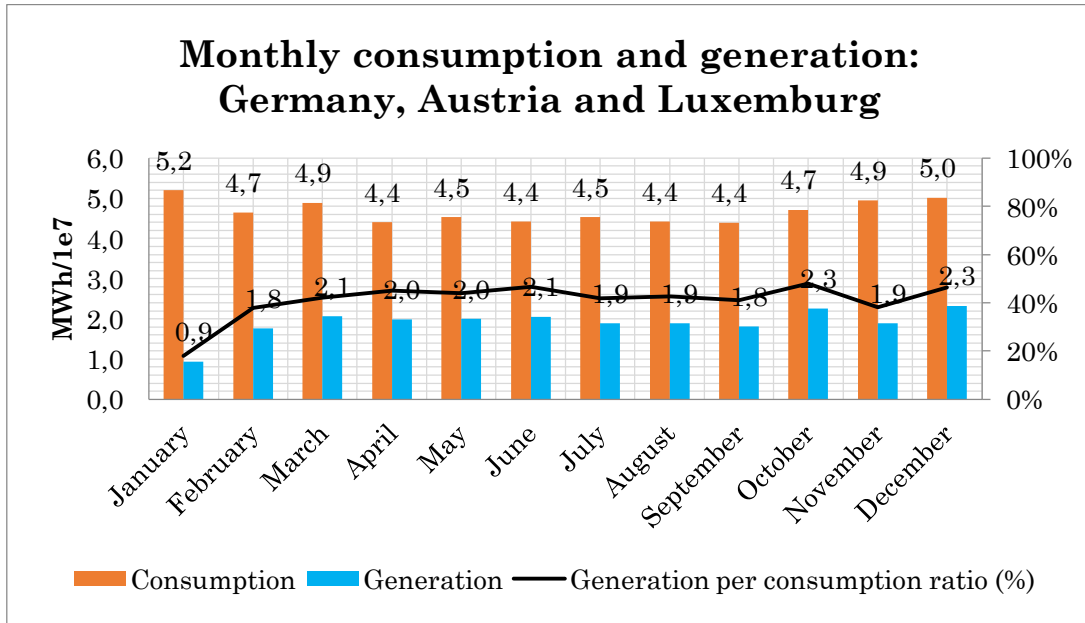


Figure 21. Monthly generation, consumption and ratio in Germany, Austria and Luxemburg.

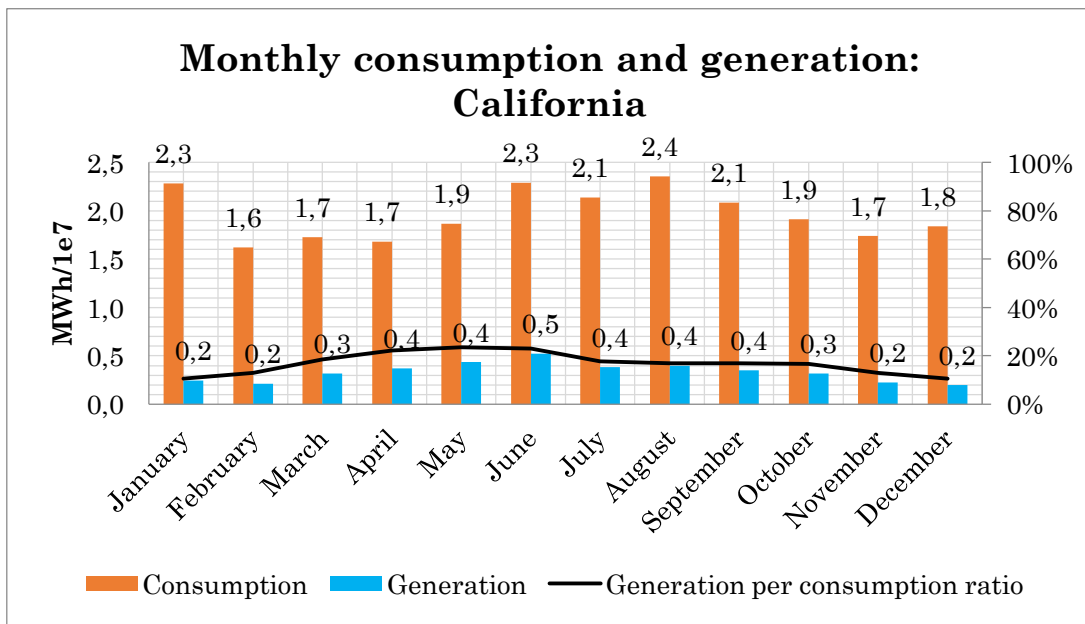


Figure 22. Monthly generation, consumption and ratio in California.

In **California**, the energy produced by solar and wind represents between 11% and 23% of the energy consumed, varying along the year. The lowest ratio happens in the winter months, specifically December and January; the highest ratio being observed in May and June. June is the month where the biggest amount of renewable energy is produced, the smallest in December. The consumption varies greatly along the year. These results are illustrated in Figure 22.

Monthly averaged power generation

In **Germany, Austria and Luxemburg** the monthly averaged generation of wind and solar power are represented in Figure 23. It is easily observed that a great variability exists in both technologies. In the case of the wind power, the most productive months are the autumn months and the beginning of winter. The month where the averaged power generated is maximum is December, followed by October and November. Wind power generation is lowest in July, August and June. On the other hand, solar generation October to February is practically derisory; most is produced from May to August. The amount produced in these months, however, is still smaller than the amount of power produced by wind generation. The monthly total amount generated, though, is relatively stable, January being the month where the smallest amount is generated, December being the month where the largest amount is generated.

In **California**, most of the energy generated comes from solar technology. In contrast with the region of Europe that is also being studied and that has been discussed in the paragraph above, monthly averaged solar is always greater than wind. The wind averaged power raises steadily from the beginning of the year to get in June at its maximum and then decrease steadily again until December, when it hits its yearly minimum. The maximum is about 3.5 times the minimum generation. Solar follows a similar pattern, the maximum is also hit in June, but in this case the maximum is about 2.5 times the minimum generation. In this case, the total amount generated varies greatly, due to the low-high-low patterns just described.

II. DAY-BASED RESULTS

Daily averaged load

In the European area studied, specifically **Germany, Austria and Luxemburg**, the daily averaged load power practically does not vary along the year. It is slightly higher as the weather gets colder, but the increase is not remarkable. These results are plotted in Figure 25.

In **California**, on the other hand, there is a genuine increase in the daily consumption during the summer months. During the rest of the year, the daily averaged power is relatively stable. These results are plotted in Figure 26.

Daily averaged power generation

The daily solar averaged power is in both cases gradually increased when hotter months come and then decreased again. In **Germany, Austria and Luxemburg** during the winter months, though, the daily averaged power generation via solar energy is almost nonexistent. The solar CF in this region was found to be 0.10. **California**, however, is a fruitful place for solar energy. Even though the production is lowered in the colder months, there is still a decent production of solar power. In this region, CF was 0.34. These data is plotted in Figure 27 and Figure 28, respectively.

Part 1: Worldwide energy demand and renewable resources

In the case of wind power, different patterns are also observed for the two areas that are object of study. In **Germany, Austria and Luxemburg**, wind is a productive resource. There is wind during basically the whole year, even though in the summer the intensity seems to decrease a little. The capacity factor for wind in this area was found to be 0.24. In **California**, the daily averaged wind power increases significantly in contrast from the rest of the year. The winter months seem to be the least productive. In this case, the capacity factor was found to be 0.28. These data is plotted in Figure 29 and Figure 30, respectively.

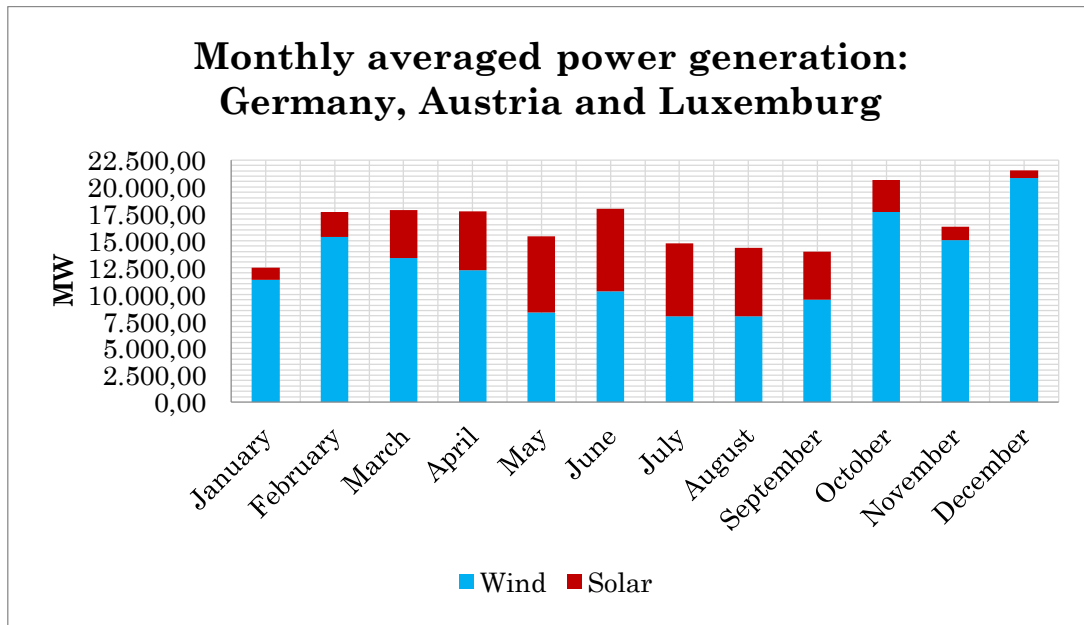


Figure 23. Monthly averaged renewable power generation for Germany, Austria and Luxemburg.

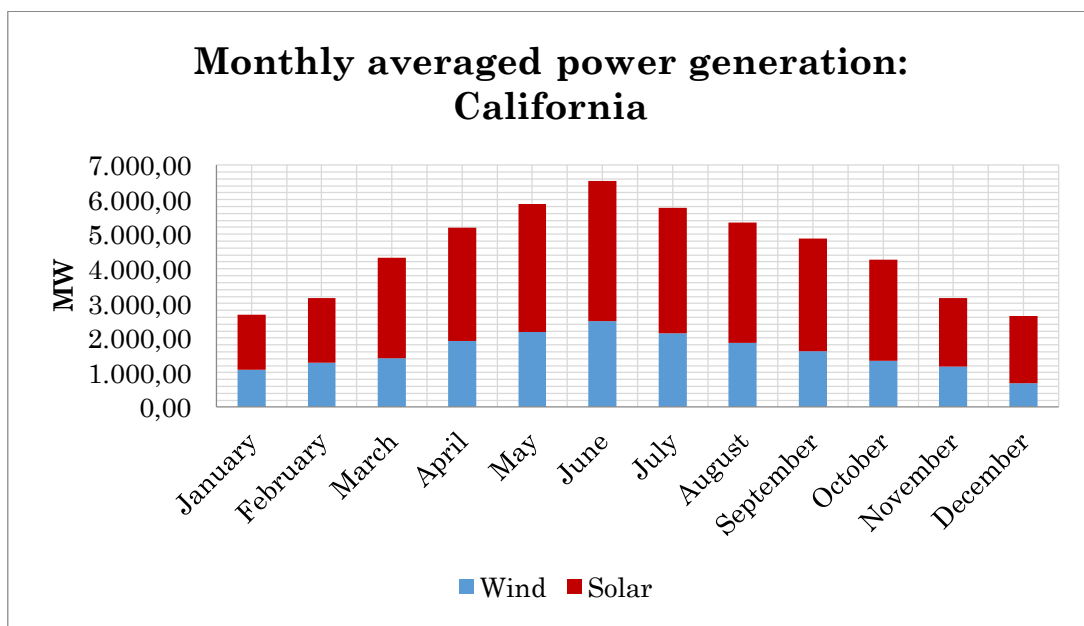


Figure 24. Monthly averaged renewable power generation for California.

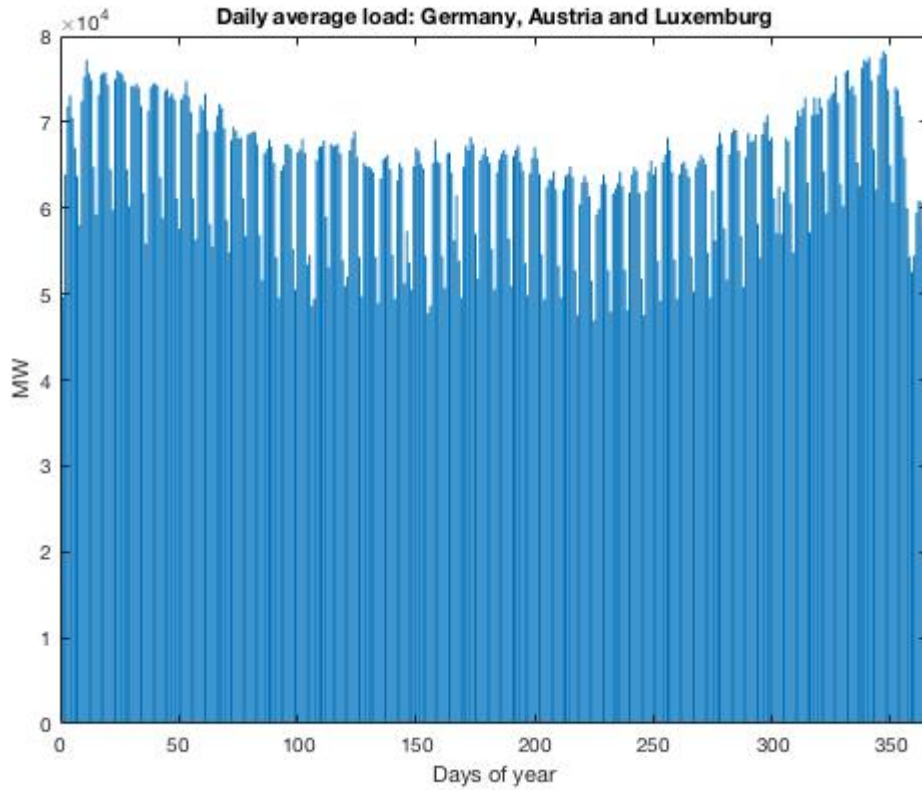


Figure 25. Daily averaged load power for Germany, Austria and Luxemburg.

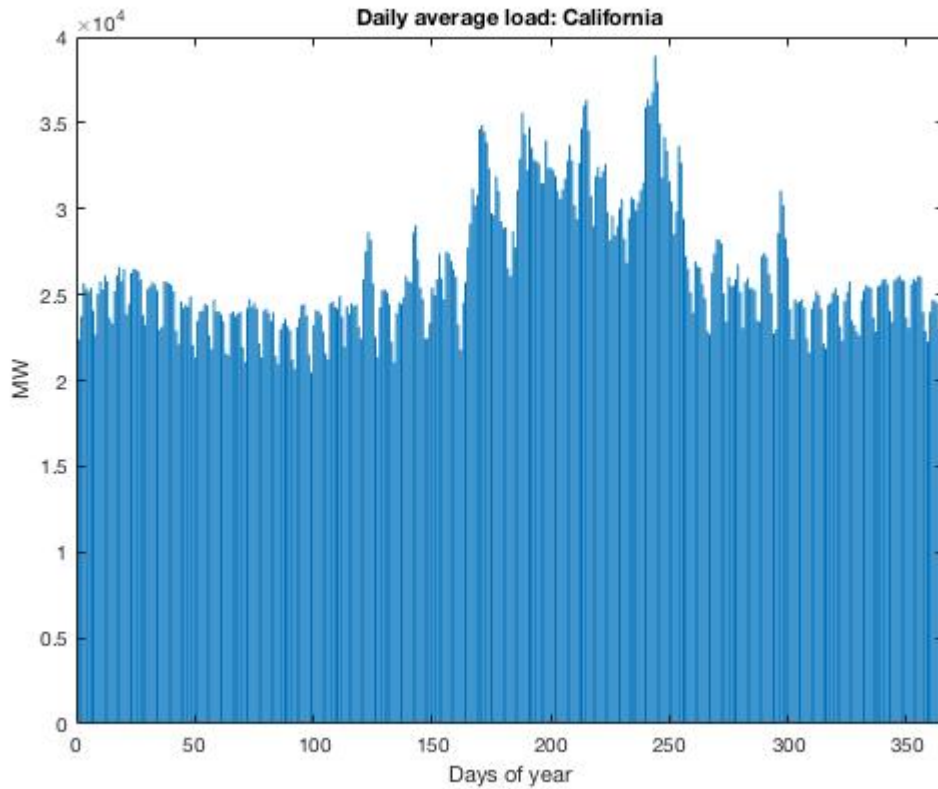


Figure 26. Daily averaged load power for Germany, Austria and Luxemburg.

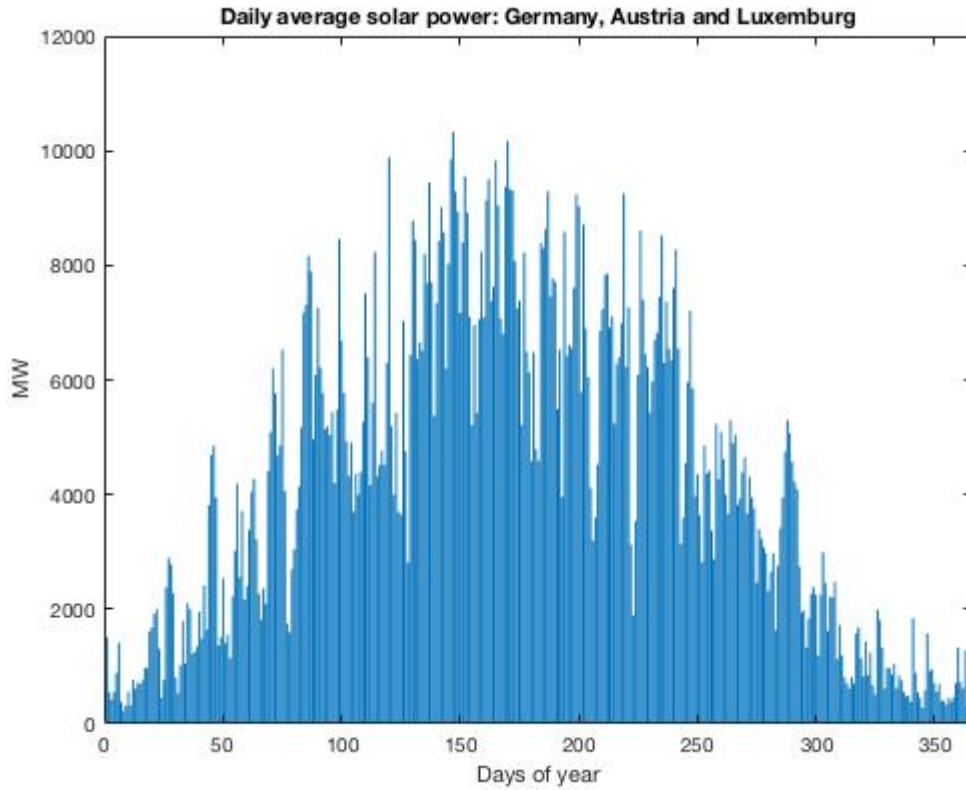


Figure 27. Daily averaged solar power for Germany, Austria and Luxemburg.

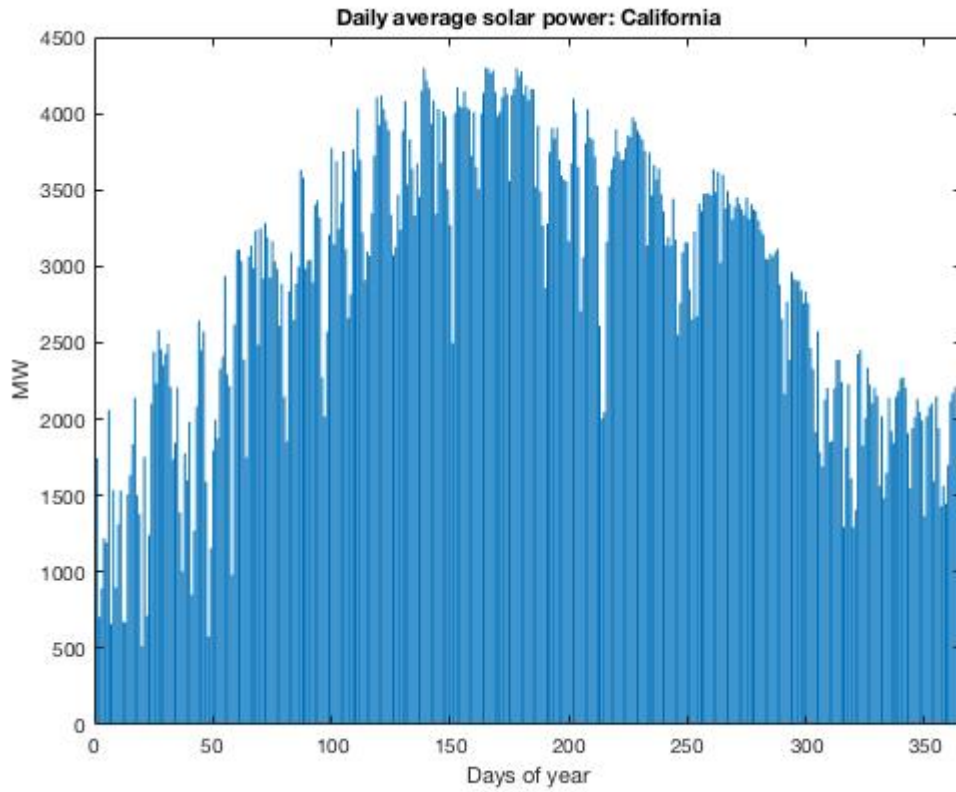


Figure 28. Daily averaged solar power for California.

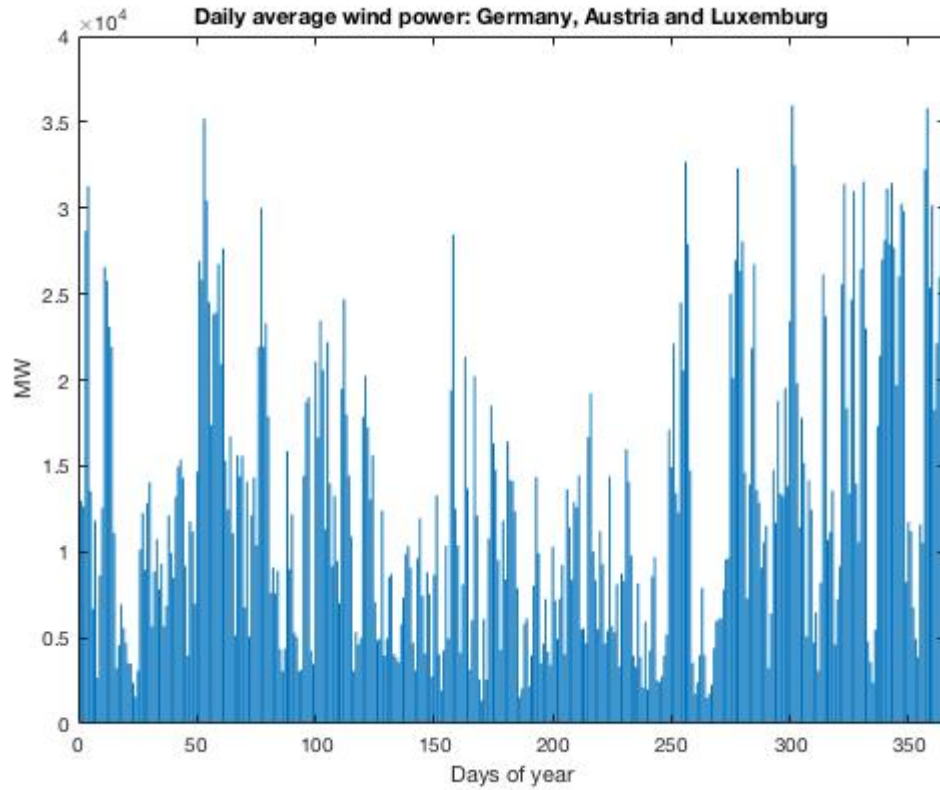


Figure 29. Daily averaged wind power: Germany, Austria and Luxemburg.

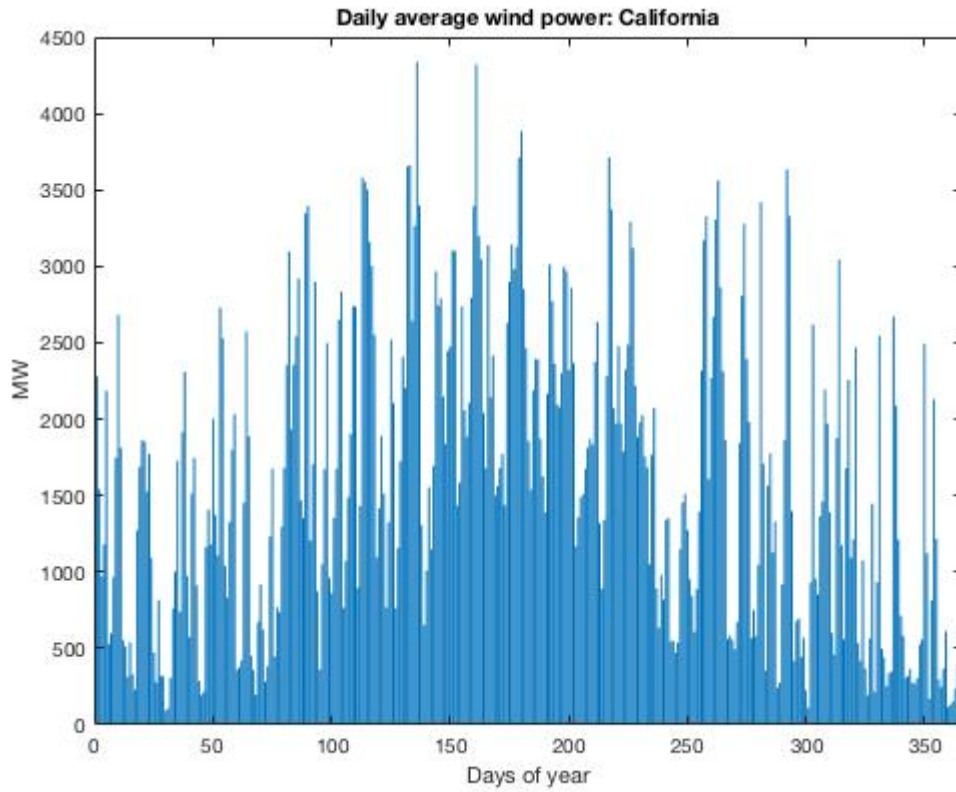


Figure 30. Daily averaged wind power: California.

1.5.5. Scaling factors and storage study

I. OBJECTIVE FUNCTION

In order to choose the best scaling factors combination, an objective function was used. It consists mainly of two addends. The first addend (a) considers each scaling factor, its corresponding capacity factor, and the cost per MWh of the technology in the region at study.

The second addend has to do with the storage that was calculated in the detailed battery calculations. It calculates a factor by dividing each storage amount by the first element of the objective function, and the average (b) of these results is obtained. This average (b) is used to divide each storage amount. This is done to obtain a value that does not mask the first element of the objective function (it would be notoriously bigger) and can be added to it. It was first considered to calculate this storage element based on battery cost, but the option was dismissed because the cost depended on such a variety of factors, that not a clear one could be calculated. The combination that gives the smallest value is the one that is going to be chosen for the next section.

$$O.F. = \underbrace{\frac{\text{scaling factor 1} \cdot \text{cost per MWh 1}}{\text{capacity factor 1}} + \frac{\text{scaling factor 2} \cdot \text{cost per MWh 2}}{\text{capacity factor 2}}}_{a} + \frac{\text{storage}}{b} \quad (3)$$

$$b = \frac{\text{storage}_1/a_1 + \dots + \text{storage}_n/a_n}{n} \quad (4)$$

The results obtained for the objective function, along with the storage amounts calculated using the detailed battery storage method previously described, and the scaled capacities, are displayed in Table 5. The shaded combinations are the ones that yielded the minimum objective function value of the options that were studied, and they are the ones that are therefore chosen for the next calculations.

Table 5. Results for the detailed calculations of storage, calculated capacities, and objective function.

		Scaling factors		Capacities (MW)			Storage (MWh)	Objective function
		Solar	Wind	Solar	Wind	Total		
Germany, Austria and Luxembourg	#11a	3.84	3.84	159,164.16	202,360.32	361,524.48	55,651,900	9,101.18
	#12a	2.63	4.26	109,010.87	224,493.48	333,504.35	110,557,700	9,233.76
	#13a	2.14	4.42	88,700.86	232,925.16	321,626.02	78,459,600	7,522.58
	#14a	1.72	4.6	71,292.28	242,410.80	313,703.08	285,335,400	13,669.15
	#15a	1.37	4.7	56,785.13	248,680.60	304,465.73	184,278,700	9,909.12
California	#11b	6.93	3.965	59,722.74	22,378.46	82,101.20	23,234,000	3,841.73
	#12b	5.88	5.88	50,673.84	33,186.72	83,860.56	25,638,500	4,286.27
	#13b	6.94	3.97	59,808.92	22,406.68	82,215.60	23,139,900	3,836.62
	#14b	7.39	3.13	63,687.02	17,665.72	81,352.74	22,708,400	3,691.26
	#15b	7.68	2.67	66,186.24	15,069.48	81,255.72	22,139,900	3,591.11

II. STORAGE STUDY

As it has just been described and as can be observed in Table 5, for **Germany, Austria and Luxemburg** the combination of SF=2.14 and WF=4.42 was chosen. Currently, the region has a solar capacity of 41,449 MWh and a wind capacity of 52,698 MWh [58], which makes a total of 94,147 MWh. With the application of the chosen scaling factors, the region would have a solar capacity of 88,700.86 MWh, and a wind capacity of 232,925.16 MWh. That makes a total renewable capacity of 321,626.02 MWh. The storage needed in this scenario was calculated and found to be 78,459,600 MWh.

A further study was done, where another scaling factor for the storage that had been calculated was tested. The results are represented in Figure 31. The curve for the calculated storage is the one marked in green. Higher and lower scaled storage variations were tested, the scaling factor used in each curve is listed in the legend in the figure. The calculated storage experiences its minimum SOC at about 10%, but if the storage is lightly shrunk, it becomes insufficient. It could be made larger in order to have higher minimums, but the option does not seem necessary. All the curves finalize at about 50%. Therefore, it is decided that the calculated storage is good already and does not need further modifications.

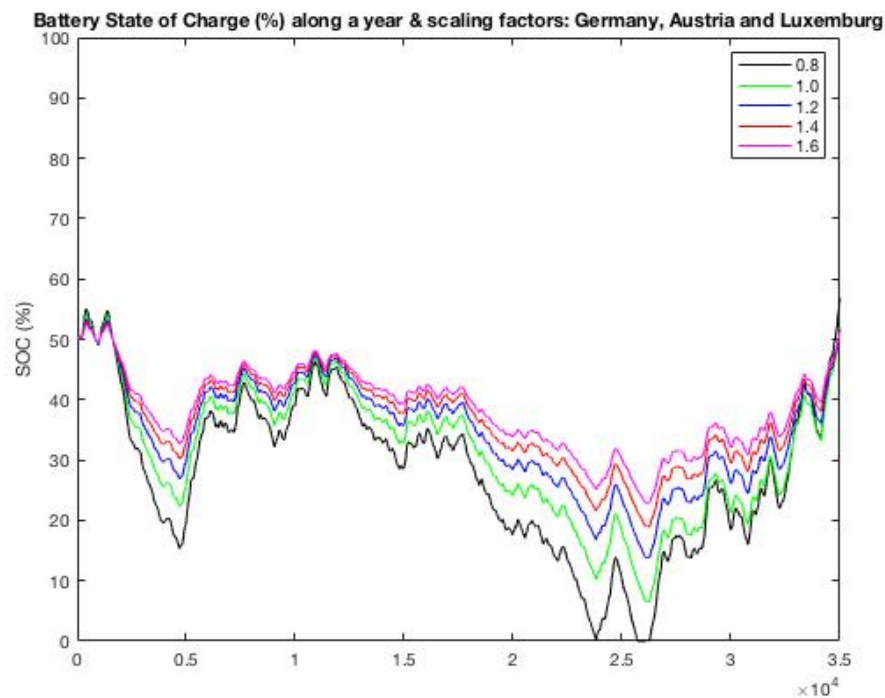


Figure 31. Storage calculated multiplied by various scaling factors. Region: Germany, Austria and Luxemburg.

For the scenario in **California**, the combination of SF=7.68 and WF=2.67 was chosen. Currently, the region has a solar capacity of 8,618 MWh and a wind capacity of 5,644 MWh [61], which makes a total of 14,262 MWh. With the application of the chosen scaling factors, the region would have a solar capacity of 66,186.24 MWh, and a wind capacity of 15,069.48 MWh. That makes a total renewable capacity of 81,255.72 MWh. The storage needed in this scenario was calculated and found to be 22,139,900 MWh.

Again, a further study was done, testing various scaling factors on the calculated storage. The results are represented in Figure 32. In this case, the curve that is obtained with the calculated storage is magenta.

Part 1: Worldwide energy demand and renewable resources

The battery is depleted quite rapidly at the beginning of the year and then, from the middle of the year, SOC is 100 for a good part of the time. Seeing this result, a smaller storage is not a good idea because it will go to both 0 and 100 even faster (black curve). A scaling factor that makes the battery bigger and that will not get SOC either to 0 or to 100 is recommended. A scaling factor of 1.2 accomplishes these requirements (blue curve). The minimum is about 6%, the maximum about 96%. SOC at the end of the year is about 54%. This additional scaling factor makes the final storage a 20% bigger than previously calculated: 26,567,880 MWh.

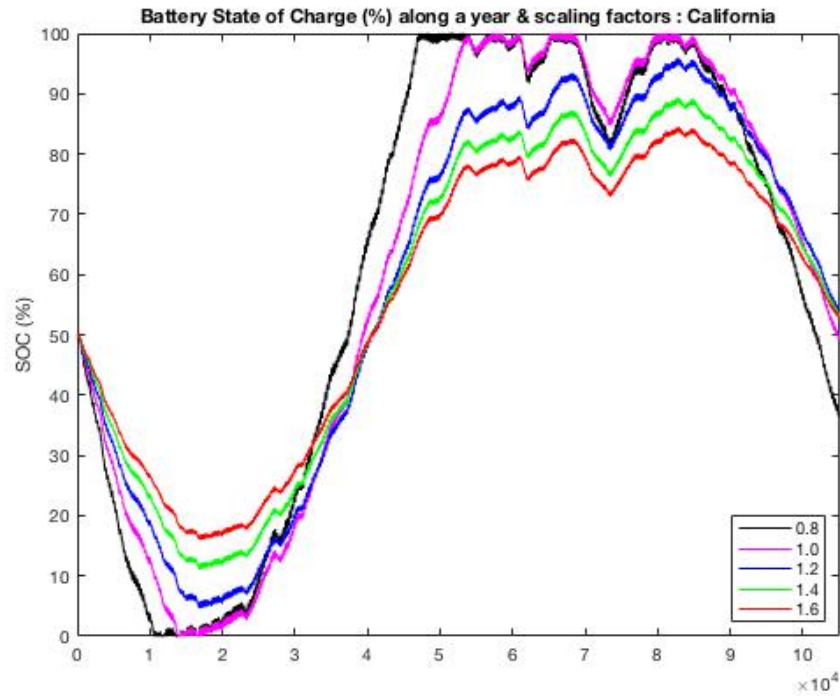


Figure 32. Storage calculated multiplied by various scaling factors. Region: California.

1.5.6. Storage for a worldwide renewable economy

The two regions previously discussed were used to make an estimation about the amount of storage that would be needed if the whole world was fueled only by renewables. This was done in the manner that is going to be described in the following paragraphs.

Since both the generation and consumption data for the two studied regions is known, it is possible to calculate, for each region, the following parameters: (1) contribution of each renewable technology in the total amount of renewably-generated energy (value between 0 and 1), and (2) consumption to calculated storage ratio. With these parameters, an equation with the general form below can be obtained for each region:

$$contribution_{solar} \cdot x + contribution_{wind} \cdot y = \frac{consumption}{storage} \quad (5)$$

Part 1: Worldwide energy demand and renewable resources

With these two equations, the unknowns x and y can be found. Thus, the following equation is obtained:

$$contribution_{solar} \cdot 9.0517 + contribution_{wind} \cdot 6.8394 = \frac{consumption}{storage} \quad (6)$$

As previously stated, the contributions in the scenarios object of study could be calculated. In the case of the worldwide estimation, the solar irradiance world map (Figure 16) and wind potential world map (Figure 17) were used to roughly determine the probable contributions of each technology in every continent based on geographical potential. The contributions used for the calculations are detailed in Table 6, along with the results for the equation above (consumption to storage ratio), consumption data, and storage, which was calculated using the calculated ratio and the consumption known from the bibliography [62]. For totals it is calculated that for a yearly consumption of 157,107,588,698.12 MWh, 19,980,954,363 MWh of storage would be required. The issues concerning the resources that would be needed in order to fabricate this amount of storage will be addressed in Part 2 of this thesis.

Table 6. Solar and wind contributions for every continent, consumption to storage ratio calculated by the previously described equation, consumption data, and storage calculated using the calculated consumption to storage ratio and the consumption data.

	Solar contribution	Wind contribution	Consumption to storage ratio	Consumption (TWh)	Storage (TWh)
Africa	0.70	0.30	8.39	9,123	1,088
America	0.45	0.55	7.83	38,541	4,919
Asia	0.50	0.50	7.95	80,866	10,178
Europe	0.30	0.70	7.50	26,951	3,592
Oceania	0.50	0.50	7.95	1,625	205
TOTAL				157,106	19,981

I. SENSITIVITY ANALYSIS

A sensitivity analysis for the worldwide storage calculation method was done. The followed process was as described: a variety of contributions was tested (from 0.1 of solar and 0.9 of wind to 0.9 of solar to 0.1 of wind). The consumption to storage ratio was then calculated, and with it and the consumption value from the bibliography, the storage was obtained. The standard deviation of these values was calculated. This process was done for every continent. The standard deviation varies, but the ratio standard deviation by calculated average continent storage is found to always be 7.67%. Therefore, the results obtained are considered acceptable as an estimate.

Part 2: Concerns surrounding energy storage technologies

2.1. The lithium-ion battery manufacturing process

The author of *Bottled lightning: superbatteries, electric cars, and the new lithium economy*, Seth Fletcher, describes in his book the battery cell manufacturing process carried out in Enerdel's lithium-ion cell factory in Indianapolis. The process begins by piping a clear liquid solvent into a mixing room, where it is combined with electrode powder—a mixture of active raw materials that make a battery run—, carbon black, and a chemical binder. Next, the mixture is painted onto long sheets of metal foil. The metal used for the anode is aluminum, while the one used for the cathode is copper. These sheets then pass through an oven for curing. Since Enerdel makes rectangular batteries, the electrode material is cut in book-size rectangles in the next step. To ensure that the surface of the electrode is clean, the sheets are brushed and vacuumed.

The next step of the process takes place in a climate-controlled dry room, where anode and cathode get sandwiched together with a separator in between. The separator is going to serve a double purpose: allow ions to pass through it, and prevent a short circuit from happening. These are dropped into plastic pouches, which are next filled with liquid electrolyte and vacuum-sealed shut. A cell is therefore obtained. In another room, the cells are precharged and then the pouch is opened to release any gas that has formed; after that, they're vacuumed and resealed. The cells are now going to be charged to 60% and left for fourteen days as a matter of quality control.

Finally, the cells are going to be wired together into a finished battery pack. The workers do this with help of assembly machines, and the cooling and heating mechanisms, the voltage-monitoring circuitry, and the thermistors that detect any individual overheating cells are added. Cells are bundled together to form modules, and modules are bundled in a case and wired with additional monitoring circuitry [10 págs. 136-137].

2.2. Composition and characteristics of lithium-ion batteries

LIBs are made of heavy metals, organic chemicals and plastics in the proportion of 5-20% cobalt, 5-10% nickel, 2-5% lithium, 15% organic chemicals and 7% plastics. The composition varies slightly between manufacturers [63]. Various authors studied the composition of lithium-ion batteries by dismantling them once they were spent. The results in percentages can be observed in Table 7.

Table 7. Composition of spent lithium-ion batteries (% mass).

Source	Co	Li	Cu	Al	Fe	Ni
Wang [1]	15.51	2.27	9.54	3.43	19.31	—
Li et al. [64]	16.00	2.00	10.00	3.00	19.00	—
Lain [65]	16.50	2.04	7.12	4.07	—	—
Dorella and Mansur [66]	29.49	3.14	16.48	8.02	—	0.02
<i>Average</i>	<i>19.38</i>	<i>2.36</i>	<i>10.79</i>	<i>4.63</i>	—	—

The theoretical cell voltage can be estimated using the following equation [4],

$$\Delta E = -\Delta G/nF \quad (7)$$

where ΔE is the voltage (V), ΔG is the Gibbs energy (J/mol), which depends on the electrode materials used [4], F is the Faraday constant (J/(V · mol)), and n is the number of electrons transferred per reaction [67]. The performance of the cell can be evaluated using parameters such as specific energy, volumetric energy, specific capacity, cyclability, safety, and abuse tolerance:

- **Specific energy or energy density (Wh/kg) and volumetric energy (Wh/L).** Amount of energy that can be stored and released per unit mass or unit volume of the battery. The energy density value can be estimated based on the battery chemistry, but the practical value will always be less due to the effect of binders, separators and other essential components in the battery [4]. Historically, increasing energy density of secondary batteries has turned out to be a quite complicated process. Currently, the energy density of lithium-ion batteries is about 150 Wh/kg [68] [69]. For application in the automotive industry, an energy density of 500-700 Wh/kg is desired [70].
- **Specific capacity (Ah/kg).** Amount of charge that can be reversibly stored per unit mass. If multiplied with the battery voltage, the value for specific energy is obtained.
- **Cyclability.** Measure of the reversibility of the lithium-ion insertion and extraction processes in terms of the number of charge and discharge cycles before the battery loses significant storage capabilities. In practice, cyclability is affected by depth of discharge (better if shallow), state of charge (better if less swing), temperature of operation (avoid very high temperatures), and battery chemistry.
- **Safety.** Battery management systems are used to prevent thermal runaways and isolate the problematic cell if necessary.
- **Abuse tolerance.** Critical requirement for practical applications, especially in electric vehicles. Abuse can be mechanical (shock and drop, roll-over, nail penetration, immersion), thermal (radiant heat, thermal stability, overheat, extreme cold) and electrical (short circuit, overcharge, over-discharge, alternative current exposure).

Lithium-ion batteries are different from other types of batteries in a variety of aspects: they do not suffer from the memory effect, in contrast with Ni-Cd batteries, and they have voltages nearly three times the values of typical Ni-based batteries. Since the voltage of a single cell is higher, the total number of cells required in a battery pack can be lowered, even though simultaneously having the same output voltage. The self-discharge rate for lithium-ion batteries is also very low, with a typical <5% per month. In the case of Ni-based batteries, this figure is about 20-30% [4].

2.2.1. Cathode materials

Lithium cobalt oxide (LiCoO₂) and lithium iron phosphate (LiFePO₄) are widely used in commercial lithium-ion batteries. Their cycle life is above 500 cycles, and LiCoO₂ can be easily manufactured in large scale and is stable in air. Its practical capacity is although quite low, about 140 mAh/g. Other problems are the high costs of the primary materials and the toxicity of cobalt.

LiFePO_4 gained popularity due to its stability, high cycle life, and temperature tolerance (-20 to 70°C). Its drawback is its low conductivity (10^{-8} cm^2/s) and relatively low capacity [71]. Its ionic conductivity is normally enhanced by either doping by ions or coating by carbon [71] [72]. Increases of a factor of 10^8 by the use of cation doping were observed by Chiang et al. [71]. Positive results on electrochemical performance have also been obtained by means of the coating strategy. Carbon coatings must be either porous or very thin to allow the easy penetration of the lithium ions, and a simple and efficient method to achieve this result should be studied. The carbon introduced in the coating, though, decreases the energy density of the material significantly, especially for the volumetric energy density. This method is considered to be overall a promising synthetic approach for future power-grade cathode materials [73].

2.2.2. Anode materials

The performance of a battery is heavily affected by the chosen anode material. Therefore, they have been extensively investigated. An example is graphitic carbon with layered structure, which has an excellent cyclability [74]. However, its theoretical maximum capacity is almost reached, which does not leave much room for improvement of its energy density. High-energy density and enhanced safety are required to meet the demands for increases in energy and power densities, especially to meet the demands from electric vehicles [75].

Tin (Sn), silicon (Si) and many other elements are known to alloy with lithium, a characteristic which makes them good candidates to replace carbon for lithium storage. These elements have the capacity of alloying and de-alloying with lithium electrochemically at room temperature. The drawback of this process is, however, the big difference in specific volume of the two forms, which could lead to substantial mechanical stress. Composites are being studied as a solution to this issue: one component, probably carbon, would perform as a stress absorber, while the other (the transition metal) would provide the capacity boost [4]. Sony announced new-generation lithium-ion batteries in 2005 which were based on this alloy/de-alloy phenomenon: the anode is made in this case of a carbon–tin–transition-metal composite, which is mainly amorphous [76].

Carbon compounds which are capable of reversible lithium ion storage are classified in graphitic and nongraphitic carbon, which is internally disordered. The latter type normally demonstrates high specific capacity, but has problems with capacity fading [77]. Carbon nanotubes are considered a good lithium host because of their high electronic conductivity, among other properties [78] [79]. Current interest is focused on carbon nanotubes and graphene composites, as they are believed to be able to achieve much higher capacities than that of pristine carbon [80] [81]. A large number of other materials are being studied for anode materials.

2.2.3. Electrolyte

A suitable electrolyte is chosen taking into account the redox environment at both cathode and anode sides, and voltage range involved without decomposition or degradation. It should also be inert and stable within a certain temperature range. Solutions of lithium salts in organic solvents are widely used as electrolytes in commercial lithium-ion batteries. Additives are widely used to assure electrolyte stability and improve the formation of good solid-electrolyte interphase.

Polymer (polymers with dissolved lithium salts), gel and ceramic electrolytes have also been developed. Polymer electrolytes are especially attractive because of their safety (low volatility), design flexibility and potential to eliminate separators. Gel electrolytes are gels with dissolved lithium salts and polar solvents, which are then added into inactive networks of high-molecular-weight polymers. Ceramic electrolytes have been studied for their applications in fuel cells for a long time, and are now being considered for use in batteries. Its main strong side is that they can be used safely in high-temperature and high-pressure environments. Ionic conductivity of ceramic electrolytes is also increased with temperature [4].

2.2.4. Separator

The function of the separator is to prevent a short circuit from happening, while allowing lithium ions in the electrolyte to pass through. A separator must obey some requirements, such as being chemically stable, inert in contact with both electrolyte and electrodes, mechanically robust, and having a pore of less than 1 μ m. The most frequently used types of separators are polymer membranes based in microporous polyolefin materials. They can be made very thin, highly porous and mechanically robust. This type of separators, if designed as multilayer composites (must have at least two functional parts: one that melts to close the pores, and one that provides mechanical strength), can also be used as a safety feature, shutting down the battery in the occurrence of a short circuit or a thermal runaway. Inorganic membranes are considered highly attractive for future high-temperature lithium-ion batteries [4].

2.3. Lithium-ion battery recycling

Due to the components they contain, batteries can be regarded as hazardous waste. When they can no longer serve any purpose, they need to be disposed of. What to do with them is a current issue, and there are a number of options, some regarded as more convenient than others:

- **Landfill:** currently, most batteries are collected by a municipal solid waste (MSW) authority and deposited in a sanitary landfill.
- **Stabilization:** a procedure that should be done before batteries are left in a landfill, to prevent its metals to be in contact with the environment. This procedure, though, is not widely used due to its high costs.
- **Incineration:** MSW sometimes send batteries to a municipal waste combustion facility. The drawback of this procedure is that components as mercury, cadmium, lead and dioxins can be emitted.
- **Recycling:** there is a large variety of recycling processes for batteries currently being studied. They will be discussed in the pertinent chapter of this thesis.

Above all, it is important to understand the environmental consequences of each method. If batteries are deposited without treatment, there is a chance that they will be in contact with liquids and some of their components may dissolve, and even though the rate at which they do so depends on the characteristics of the situation, there is a real possibility that this situation may lead to serious contamination of ground and water [82].

Battery recycling is becoming more popular due to the rising importance of batteries and thus the necessity of taking care of its disposal and reuse of its components, some of which could be considered

relatively critical resources. A number of problems, though, arise. The recycling process needs to be efficient in a way that its final product is economically feasible of making it into the market, and needs to be less harsh on the environment than the extraction itself [83]. Additionally, the batteries need to be treated before entering the recycling processes. When a LIB is no longer functional, a little residue power still remains [84]. LIBs often blow up during the recycling process due to radical oxidation when a lithium metal produced from a battery overcharge sustains a mechanical shock from exposure to the air [85]. Therefore, to prevent short-circuiting and self-ignition, spent LIBs are often discharged before starting with the recycling process [66] [86] [87], normally by placing them in a salt solution. They then need to be dismantled.

Recycling processes evaluated by the European Portable Battery Association (EPBA) have proved that mercury-free manganese-alkaline and zinc-carbon batteries can be recycled in metallurgical processes [82].

There is research going on in the field of recycling batteries, but it is mainly focused in recovering only some particular components of the battery –such as cobalt and nickel– which means that one should still dispose of the rest [83].

2.3.1. The battery recycling process

The battery recycling process can be divided into pretreatment stage or primary treatment stage, which normally involves physical processes such as the crushing of the dismantled battery to improve the efficiency of the process. The secondary treatment stage is carried out using chemical processes –solvent extraction, precipitation, electrowinning, crystallization, calcining–, and will be dealing with the cathode or anode materials. In this stage, some metals, such as copper (Cu), aluminum (Al), cobalt (Co), lithium (Li), nickel (Ni) and manganese (Mn) can be recovered from the leaching solutions. The general secondary treatment stage is schematized in Figure 33. It is also known as conventional deep recovery process of spent LIBs [1].

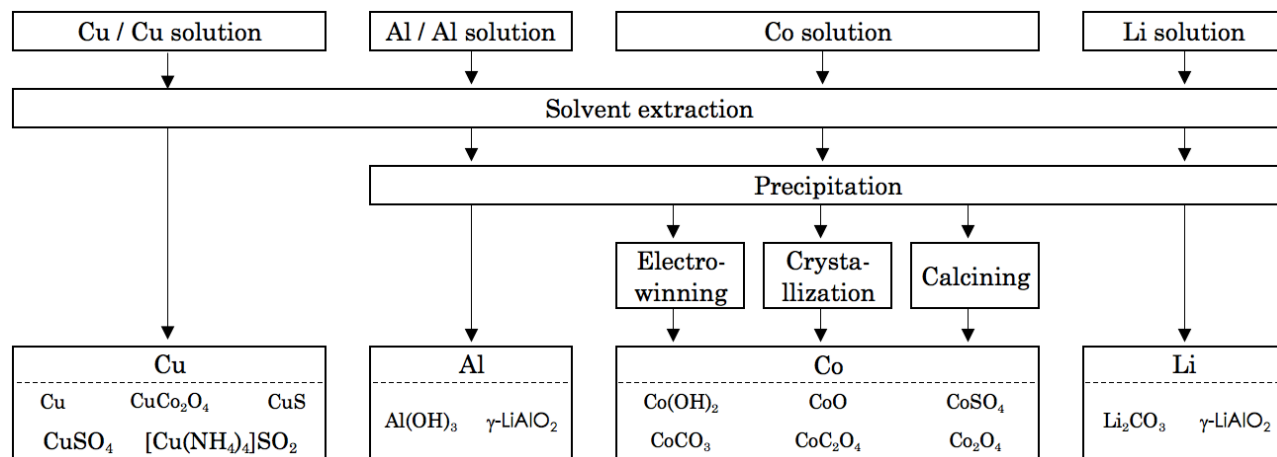


Figure 33. Schematization of the deep recovery processes for the different elements present in LIB batteries. At the lower level of the scheme, the compounds below the discontinuous line are the forms in which the element of interest (element above the discontinuous line) can be recovered.

Even though lithium-ion batteries are generally considered more innocuous than other types of batteries, there are still a number of considerations that need to be taken into account.

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The first step of any recycling process is the dismantling and separation of parts of a spent battery. Metal recovery will be possible thanks to chemical processes, but to ensure their maximum efficiency, physical and mechanical processes need to be firstly used: skinning, removing of crust, crushing and sieving, followed by a separation of some kind. This way the cathode materials are obtained [5].

During the dismantling, certain safety precautions must be paid attention to, especially when the process is done manually. One example would be the study done by Dorella and Mansur in 2007, which focused on recovering the cobalt of a battery, and used the following procedure: firstly, the plastic cases of the batteries were removed using a small knife and a screwdriver; secondly, the metallic shell was removed with a saw, after using a cryogenic method (immersing it in liquid nitrogen for 4 minutes and then fixing it in a lathe). Then, using pliers, the internal material of the battery was removed. At this point the anode and cathode could be uncurled. They were separated and dried for 24 hours at 60°C. General safety for the process included gloves, glasses and gas masks [66].

I. PHYSICAL PROCESSES

These include mechanical and thermal treatments. The distinct properties of the elements, such as their density, conductivity, or magnetic behavior, are what makes possible a specific component be separated [88]. They are most often used as a pretreatment for the chemical processes; this way, specific components can be recovered and treated individually. Thermal treatments include all of those that rely on physical state changes or reactions promoted by heat [5]. An example would be the process done by Castillo et al., who purified a residue consisting of iron, cobalt, nickel and traces of manganese trihydroxide ($\text{Mn}(\text{OH})_3$) from carbon and organic compounds by calcining them in a furnace at 500°C during 2 h. The alloy can then directly undergo beneficiation in metallurgical applications [89].

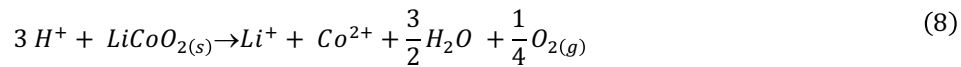
Ultrasonic treatment yielded effective results in separating the cathode material from the aluminum foil. By simultaneously combining agitation with ultrasonic treatment, almost all electrode materials were separated. However, it is thought that the effect of cavitations consequence of the ultrasonic waves can make some substances scatter in the water. To apply this treatment, the battery should be crushed first [1].

II. CHEMICAL PROCESSES

This category includes acid and base leaching, precipitation, extraction and filtration, among others. The metals are first dissolved in a solution (be it acid or alkaline), so they can be precipitated in various ways, some being altering the pH of the solution, adding reaction agents, or by using electrolysis. That way, a purified product is obtained. Another method is to extract the metal using an organic solvent, and then using the techniques mentioned before to precipitate it.

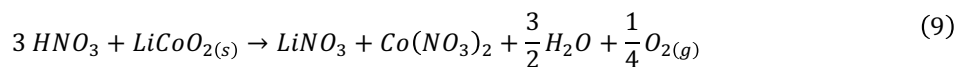
- **Acid leaching.** A hydrometallurgical process. It is mainly used to transfer the metals contained in dust separated from plastic, iron scraps and paper residues in preliminary treatment steps. The leaching of powdered LiCoO_2 from LIBs is normally done using strong inorganic acids, such as sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and nitric acid (HNO_3) [5]. The leaching rate of cobalt and lithium highly depends on the leachant concentration, temperature, reaction time and solid-to-liquid ratio. The reaction that takes place in this process can be described with the following reaction [1]:

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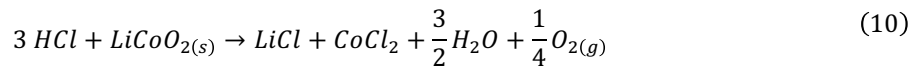


Extraction of cobalt is the most challenging in this case. Using only HCl or HNO₃, efficiencies higher than 85% can be achieved, but if using H₂SO₄, an oxidizing agent, such as hydrogen peroxide (H₂O₂) needs to be added in order to achieve a high efficiency. This leaching process is done at 75-80°C [5] because of the higher solubility of LiCoO₂ in the solvent at higher temperatures [1]. Depending on the acid used, the procedure to then recover the metals is going to differ:

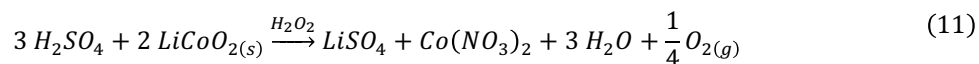
- *Nitric acid (HNO₃):* LiCoO₂ is first dissolved in HNO₃, the solution heated. Distilled water needs to be added continuously to maintain the appropriate pH value of 2.6 [1]. Cobalt is later going to be recovered by electrochemical methods (transform it to cobalt hydroxide and then to cobalt oxide by dehydration, as described in electrochemical processes below) [5]. For the lithium solution, evaporation and crystallization processes may be used. Kondás et al. developed a process on this to be used in Li/MnO₂ batteries [90]. The reaction that takes place is the following [1]:



- *Hydrochloric acid (HCl):* After leaching the battery active material with hydrochloric acid, the solvent PC-88^a is used to separate cobalt. After that, the best possible option was found to be to use a 1M sodium oxalate (Na₂C₂O₄) solution to precipitate it (cobalt recovery of 99.5%). Other precipitators may be used, but this one yielded the best results because CoC₂O₄ is easy to separate and filtrate. Lithium in the filtrate was precipitated as lithium carbonate (Li₂CO₃), using a saturated sodium carbonate (Na₂CO₃) solution in excess (lithium recovery up to 94.5%). The leaching reaction is described as [1]:



- *Sulfuric acid (H₂SO₄):* Before starting the acid leaching process, the cathode is leached with sodium hydroxide (NaOH) to remove Al [1]. Then, the leaching process is done in an oxidizing environment –hydrogen peroxide (H₂O₂) is added to the solution–, sulfuric acid leaching will transfer cobalt and lithium to the aqueous solution [91]. An important variable for the metal dissolution was found to be the concentration of hydrogen peroxide in the solution, as opposed to the temperature or the concentration of acid. The reaction that occurs is, in this case, the following [1]:



Next, NH₃·H₂O will be used to precipitate aluminum, and Cyanex 272 to separate cobalt. Crystals of cobalt sulfate (CoSO₄) will be obtained by submitting the acidic solution obtained by first leaching the battery residues with H₂SO₄ and H₂O₂ to crystallization (by evaporation). At 90% of water evaporation, 70% of cobalt was crystallized. Percentage of

Part 2: Concerns surrounding energy storage technologies

water evaporation must be optimized considering that the solid phase contamination will increase as the percentage of water evaporated increases [91].

- **Bioleaching.** The biological counterpart of the traditional hydrometallurgical process discussed above, acid leaching, which is increasingly being used due to its higher efficiencies, lower costs and fewer industrial requirements [5] [92]. The process consists in extracting metal cations from insoluble ores by biological oxidation and complexation processes. It is mainly used for copper, cobalt, nickel, zinc, and uranium [93]. Mishra et al. Demonstrated in 2008 that it was possible to dissolve metals from spent cathode material of LIBs by the use of acidophilic bacteria, which use the elemental sulfur and iron contained in the medium as their energy source. A culture of *Acidithiobacillus ferrooxidans* produced sulfuric acid, which produced the metals to be indirectly leached. Cobalt was leached faster than lithium [92].
- **Solvent extraction.** A number of studies to recover certain metals from spent lithium-ion batteries (LIBs) using various solvents have been performed. Kang et al. Recovered 92% of pure cobalt sulfate from spent LIBs using bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) [94]. In another study, Nan et al. demonstrated that cobalt, copper and lithium could be effectively recovered and reused, and the recovered products have a high purity. Their process consisted in leaching the internal substances of the battery with an alkaline solution and dissolving the residues with H_2SO_4 . This was followed by a precipitation of cobalt as an oxalate, and then the extractants Acorga M5640 and Cyanex 272 were used to extract the small quantities of copper and cobalt, respectively. Over 98% of copper and 97% of cobalt were recovered. Recovery of lithium was done by precipitating it as lithium carbonate. The treatment cost could be reduced by using a machine to dismantle the batteries and by recycling the extractants with sulfuric acid; the waste solutions were not hazardous. For these reasons the process was believed to be feasible for large-scale recycling of spent LIBs [95].
- **Precipitation.** Use of precipitating agents to separate a component present in a solution. This is, as seen in the previous concept, something that is normally used after the metals have been extracted from a substance or material and are in solution. Once the precipitation has occurred, it is fairly simple to separate it of the solution by means of filtration. Precipitation equilibrium must be taken into account, because some of the complexes formed can be partly dissolved, and partly deposited at the bottom of the container in solid form. Normally, the pH of the solution is adjusted in order to precipitate as much of the complex as possible.
- **Electrochemical processes.** Myoung et al. prepared cobalt oxide (Co_3O_4) from Co(III) obtained from waste $LiCoO_2$ cathodes by applying electrochemical deposition and appropriate thermal treatment. Interest in cobalt oxide is due to the fact that it is considered to be a promising electrochromic compound. In order to be able to apply the electrochemical treatment, $LiCoO_2$ first needed to be separated from the cell and dissolved in nitric acid (HNO_3), the solution heated to increase the solubility of the compound. A -1.0V potential was applied for the formation of cobalt

hydroxide ($\text{Co}(\text{OH})_2$), which was formed by electrochemical deposition³ on the titanium surface. The obtained film was then subjected to thermal treatment of 400°C to (1) evaporate hydration (physically-absorbed) water, and (2) transform cobalt hydroxide into cobalt oxide (Co_3O_4) [96]. The use of electrochemical techniques has the advantage that these are highly selective, thus rendering a high purity product, but the drawback is that they consume too much electricity [5].

III. EXAMPLES OF RECYCLING PROCESSES

Shin et al. [63] studied and proposed a process for the recycling of lithium-ion batteries, which they claimed to be possible to apply in a commercial scale plant. The process includes mechanical separation of lithium cobalt oxide particles and utilizes a hydrometallurgical procedure for the recovery of lithium and cobalt. Its flowchart can be observed in Figure 6. The effects of hydrogen peroxide in leaching, as well as the effects of incineration, were studied. It was found that a 15%vol of hydrogen peroxide (H_2O_2) in sulfuric acid leaching was enough for a full recovery of lithium and cobalt. H_2O_2 helps in leaching because the chemical bond between cobalt and oxygen is very strong, and that makes the acid leaching process difficult. By adding H_2O_2 , cobalt (III) is transformed to cobalt (II), and the leaching efficiency is increased. On the other hand, incineration is not recommended. This procedure was first considered because the particles obtained from crushing and mechanical separation include carbon and organic binder, which creates problems in the filtration process. By incinerating the particles in a furnace at 900°C for one hour, both carbon and organic binder are removed. However, it was found that the leaching efficiency of cobalt after incineration is significantly lower because the surface of the lithium cobalt oxide is covered with molten aluminum.

Contestabile et al. studied another process for the recycling of lithium-ion batteries [97]. A flowchart of the process can be observed in Figure 35. Their main concern was cobalt recovery and further synthesis and testing of a cathode with the recycled cobalt. The separation of active materials was done selectively using N-methylpyrrolidone (NMP). The spent batteries were treated at about 100°C during one hour. With this the films were effectively separated from their support and copper and aluminum could be recovered in their metallic form by means of filtration. After cleaning, these metals can be used directly. The rest of the electrode film components were recovered by decantation of the separated powders and repeated water washing. NMP can be recovered and reused many times due to its high solubility for PVDF (polyvinylidene fluoride, the binder). The residual powders were then treated with a small volume of HCl (hydrochloric acid) 4 M at about 80°C for one hour. The total dissolution of cobalt and lithium was achieved by using an acid/sample ratio of approximately 10. The carbon powder precipitated and could be separated by decantation. The cobalt dissolved in HCl is then recovered as cobalt (II) hydroxide ($\text{Co}(\text{OH})_2$) by adding one equivalent volume of a 4 M NaOH solution. Industrially, the process could be easily controlled by using a pH sensor: the precipitation of the compound begins at $\text{pH} = 6$ and can be considered complete at $\text{pH} = 8$. $\text{Co}(\text{OH})_2$ can then be easily separated and recycled, and was used to synthesize lithium cobalt oxide to be tested as a cathode in

³ Electrochemical deposition is a synthesis method described by the Royal Society of Chemistry as a process where a film of solid metal is deposited from a solution of ions onto an electrically conducting surface (an electrode). Three electrodes are required (working, counter and reference), and when sufficient current is passed through the solution, metal ions are reduced at the working electrode. It is also known as electroplating or cathodic electrodeposition [143].

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a common LIB configuration. The electrode was characterized by galvanostatic cycling and cyclic voltammetry. It was found to have good working capabilities, which concludes that recycled material can be successfully used to manufacture new batteries.

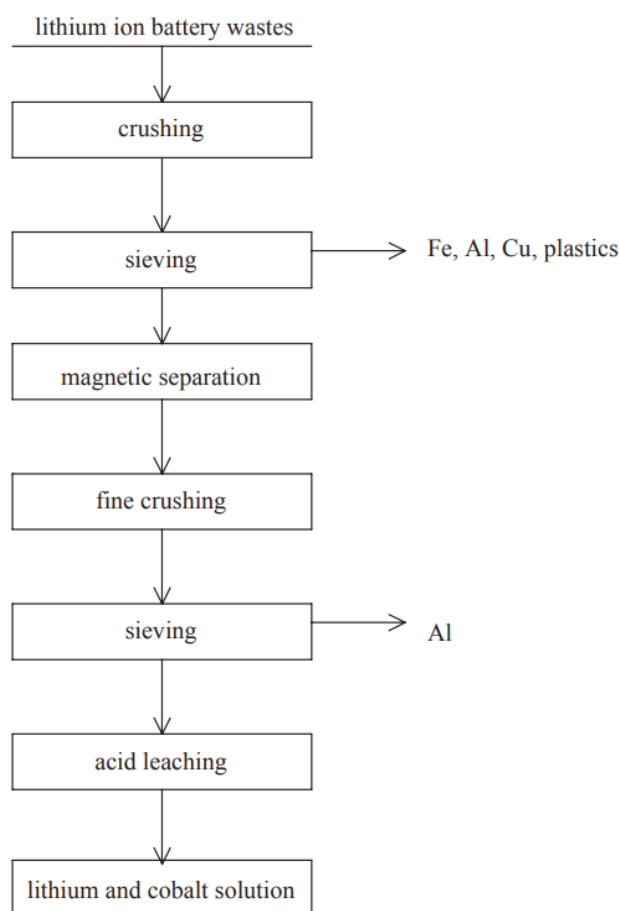


Figure 34. Flowchart for the battery recycling process proposed by Shin et al.

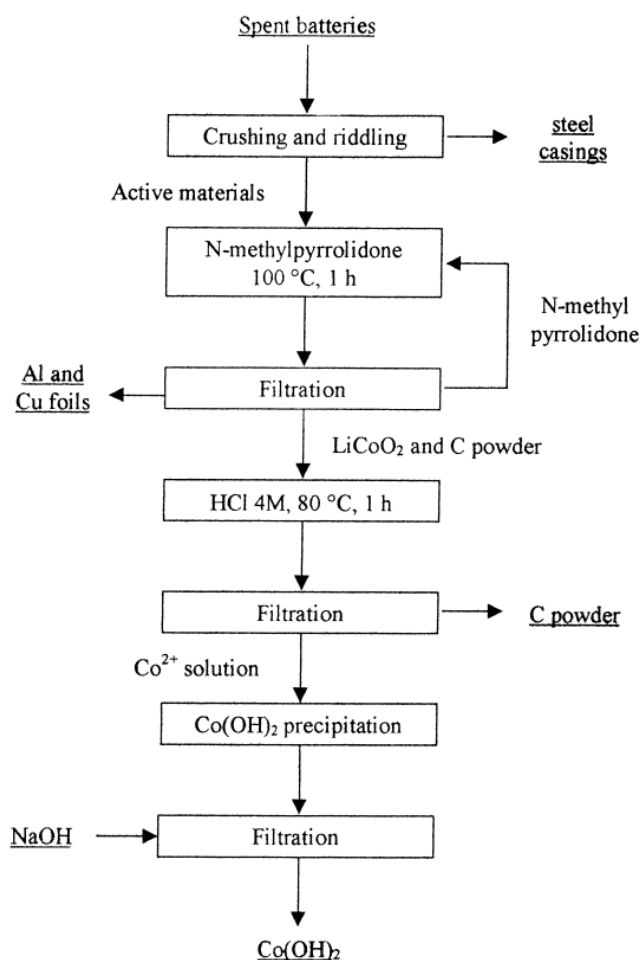


Figure 35. Flowchart for the battery recycling process proposed by Contestabile et al.

Lee and Rhee [98] developed a recycling process for LIBs (Figure 36) involving mechanical, thermal, hydrometallurgical and sol-gel steps, which was demonstrated that could be used to synthesize lithium cobalt oxide. Firstly, a mechanical and thermal treatment was applied to concentrate the electrode active materials in a powder form. It consisted of a thermal treatment at 100-500°C for 30 min, high-speed shredding to 5-20 mm, followed by a second thermal treatment at 300-500°C for 1 h, a vibrating screening, and finally a calcinations at 700-900°C for 1 h, where carbon and binder are burnt off above 800°C. The second phase involves grounding the active material in a ball mill and drying it in an oven at 60°C for 48 h, and then leaching it with acid to dissolve cobalt and lithium. The authors found that the optimal conditions for the process were to use 1 M HNO₃, with 1.7%vol H₂O₂, 75°C as the operating temperature, 20 g of solid per liter of solution, and treatment of 1 h of duration. The last phase concerns the preparation of LiCoO₂ (lithium cobalt oxide) powder and characterization. The amorphous citrate precursor process was used, and a powder with a large specific surface area was produced. In this process, the Li:Co ratio in the leach liquor was adjusted to 1.1 by adding a LiNO₃ solution, followed by an equivalent volume of 1 M citric acid solution: a gelatinous

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precursor was obtained. This precursor was treated at 950°C for 24 h and a purely crystalline LiCoO₂ was obtained. The quality of the product obtained was tested, and capacities over 90% of those for LiCoO₂ used in the battery industry were observed for the first cycle. After 30 cycles, both charge and discharge capacities decreased by less than 10% compared to the values on the first cycle. The authors thus concluded that the cathode active material prepared from spent LIBs had good charge-discharge capacities and cycling performance.

Zhang et al. [99] developed, in 1998, what could be possibly considered one of the first recycling processes for lithium-ion secondary batteries, which were focused on cobalt and lithium separation and recovery. The process, which flowsheet can be observed in Figure 6, consisted on the leaching of the anode materials of the LIB batteries, the separation of cobalt from lithium by means of solvent extraction, and the precipitation of lithium as carbonate. They experimented with different concentrations and types of leachant, temperature, reaction time and solid-to-liquid ratio. They found that hydrochloric acid produced the best results, with a leaching efficiency greater than 99% of cobalt and lithium when using a 4 M HCl solution at 80°C during 1 h. They extracted the cobalt in the leach liquor selectively using 0.9 M PC-88A extractants in kerosene, then recovered it as high-purity cobalt sulfate. After this process, the cobalt had been removed from the leach liquor, but the lithium was still there. The solution was concentrated and the lithium was recovered as lithium carbonate precipitate by the addition of a saturated sodium carbonate solution at almost 100°C. The content of cobalt in the lithium precipitate was less than 0.07%. Lithium recovery was almost 80%.

Nan et al. [95] later developed a similar process in which they leached the active materials with an alkaline solution and then dissolved the residues with a sulfuric acid solution. Afterwards, about 90% of the cobalt was deposited as high-purity oxalate and the extractants Acorga M5640 and Cyanex272 were used to extract the small quantities of copper and cobalt, respectively. Overall, recovery of copper and cobalt were about 98% and 97%, respectively. Lithium was recovered as lithium carbonate, as done in the process in the previous paragraph. The waste solution was treated innocuously. The recovered compounds were used to synthesize LiCoO₂ for the cathode, and found to have a good electrochemical performance. The authors claim this recycling strategy is feasible for LIB recycling in large-scale, since the dismantled was done using a specially designed machine, and that, as well as the cobalt recovery as oxalate, notoriously lowered the overall cost of the process. The extractants used could also be stripped with sulfuric acid and reused.

Lain from AEA Technology (UK) presented a process in 2000 aimed at recovering every component of the lithium-ion cell [65]. The process is done at ambient temperatures and is composed of three main stages: electrolyte extraction, electrode dissolution, and cobalt reduction.

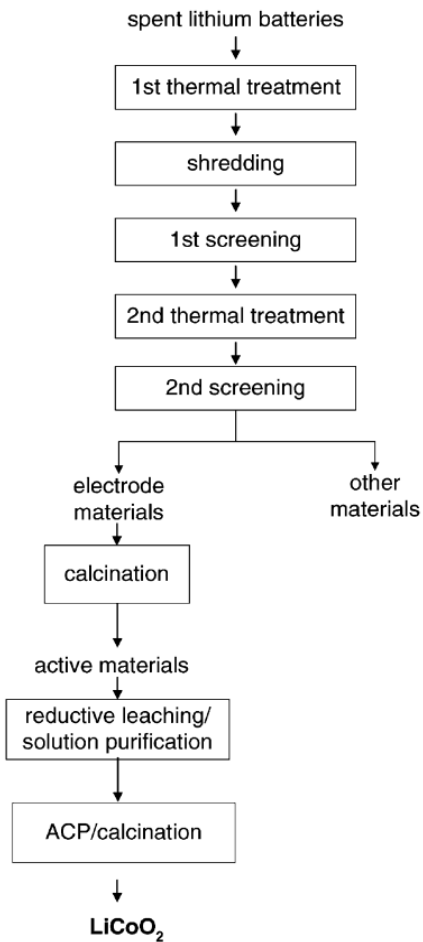


Figure 36. Lithium-ion batteries recycling process proposed by Lee and Rhee.

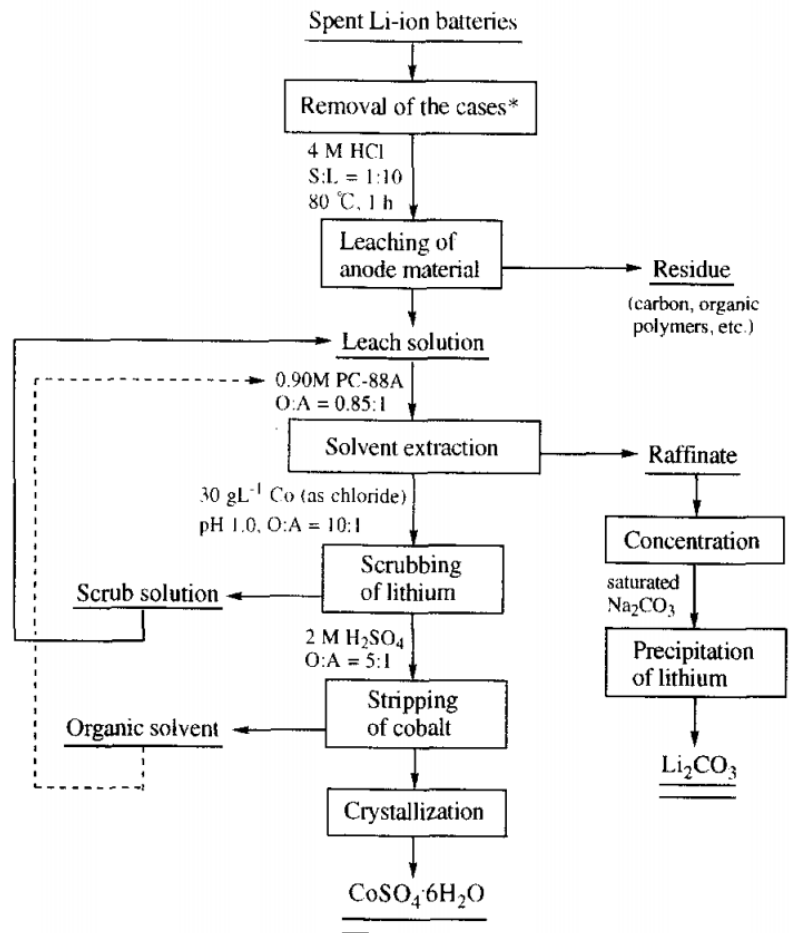


Figure 37. LiCoO_2 obtention process from spent LIBs proposed by Zhang et al.

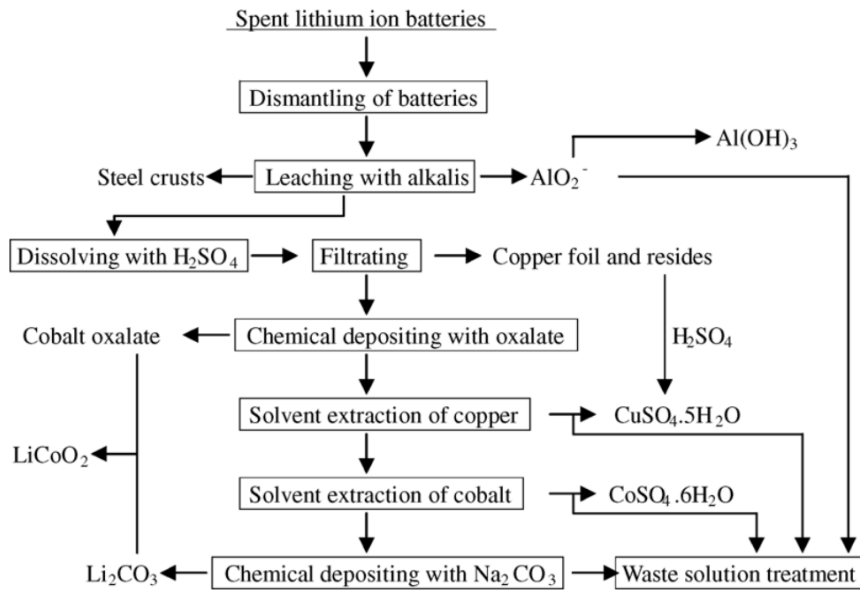


Figure 38. Lithium-ion batteries recycling process proposed by Nan et al.

2.4. Resource concerns

Lithium and cobalt, metals used in the structure of lithium-ion batteries, are considered rare. Therefore, their supply may become complicated in the future. Even though there may be enough mined quantity to meet the world demand, political stability and social and economical issues could play a role in the shortage of these metals.

2.4.1. Lithium

Lithium is used in batteries, but it is also employed for making highly durable and light-weight alloys, in heat-resistant glassware and ceramics, lubricants, air conditioning and nuclear reactor coolant [100]. Lithium carbonate (Li_2CO_3), lithium citrate ($\text{C}_6\text{H}_5\text{Li}_3\text{O}_7$) and lithium sulfate (Li_2SO_4) are used to treat bipolar disorder [101]. A pie chart illustrating the share of the various applications of lithium can be observed in Figure 39.

In 1975, the U.S. Geological Survey (USGS) warned of an impending shortage of lithium for the year 2000 on, but at that point, this lithium was only intended to be used in nuclear reactors. The world then started looking for more lithium deposits and, after the 1975 conference, data on lithium abundance multiplied. After this, there seemed to be little to worry about [10 págs. 150-153]. The metal later became important for energy storage and the concerns have begun to rise again. The U.S. Geological Survey estimated the world resources of lithium in their 2017 report as more than 53 Mt [102]. The detail of the location of the resources can be observed in Table 8.

Approximately 40% economically viable reserves of lithium are located in Bolivia, under the control of Evo Morales

[100]. Its Salar de Uyuni is thought to contain the world's single largest lithium resource, estimated at some 8.9 Mt [10 pág. 157]. This was discovered in 1981, but at first no one paid attention to it. After the first electrical vehicles were announced, though, everyone became suddenly interested in lithium and, Bolivia and its citizens, in its position of one of the poorest countries in the America, decided they would fiercely defend their lithium resources, after a history of natural resources exploitation mostly at hands of foreign interests without contributing anything to Bolivians. With Evo Morales brought to the power, the relations between Bolivia and the United States deteriorated, but it was clearly and sharply stated that if any foreign business was interested in the Bolivian lithium reserves and it was given access to the Salar de Uyuni, it had to build

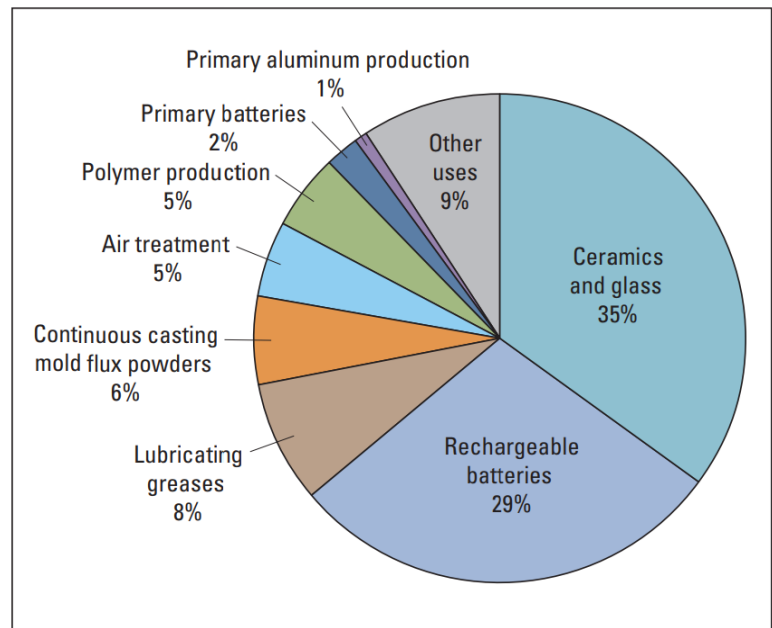


Figure 39. Pie chart showing major end uses of lithium as a percentage of world consumption in 2013. Chart extracted from USGS "Chapter K. Lithium" in Critical Mineral Resources of the United States – Economic and Environmental Geology and Prospects for Future Supply.

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an electric-car industry in Bolivia. If no one would agree with this, the country would be developing the lithium reserves on its own, no matter if it took longer that way. The Bolivian project for exploiting lithium was eventually started, but the political issues around it and its leader are bringing its development difficulties [10 págs. 172-176]. According to the Bolivian writer Juan Carlos Zuleta, there are at least three challenges to be overcome: political (conflicts of interest and shady truths), logistical (low evaporation rates, high magnesium-to-lithium ratio, and lack of easy access to the sea), and social (the local communities demand that the government do something about the region's poverty as a condition for harvesting their lithium) [10 págs. 189-190]. On the other hand, USGS and Bolivia do not agree on the quantity of lithium that the Salar de Uyuni contains [10 págs. 172-176].

Some geologists, K. Evans among them, suggest that lithium deposits outside of Bolivia are larger than estimated by the U.S. Geological Survey [100]. Potential sources of lithium are from pegmatites, continental brines, geothermal brines, oilfield brines and the clay mineral hectorite. The most significant quantities of pegmatite are located in North Carolina (2,830,000 t Li), Zaire (2,300,000 t Li), Russia (1,000,000 t Li) and China (750,000 t Li); most of the resources found in brines are in Salar de Atacama in Chile (6,900,000 t Li), Salar de Uyuni in Bolivia (5,500,000 t Li), China and Tibet (2,600,000 t Li), and Salar de Rincon in Argentina (1,860,000 t Li); in the case of hectorites, the location is the McDermitt Caldera in Oregon/Nevada (750,000 t Li) [103].

The Salar de Atacama, in Chile, is the world's purest and most productive lithium source. There are two lithium operations located in this area, the largest of which is operated by the Sociedad de Química y Minera (SQM). This Salar actually used to belong to Bolivia, but was lost in the War of the Pacific (1879-1884). SQM's business started in 1996 by selling potassium to make fertilizer. Even though lithium was also sold, it was only extracted as a byproduct at that point. In 2008 lithium demand began to increase and SQM was soon supplying 31% of the world's demand. Its main market has although continued to be fertilizers. The company claims that in the Salar de Atacama there are 40 Mt of economically extractable lithium carbonate equivalent, 190 Mt in total. The current capacity is 40,000 tons per year [10 págs. 181-186].

The economic feasibility of recovering lithium depends on the size of the deposit, its lithium content and content of other elements, and the processes used for purification of the metal [104]. Depending on the degree that these factors are known, deposits are classified as a reserve or as a resource. This classification may, therefore, vary due to the obtaining of new information and the changes in prices.

Some studies have been done to evaluate the feasibility of the increasing amount of lithium being used, considering that lithium is regarded as a rare metal. One of these studies was done by Gruber et al. in 2011 [104]. Their comprehensive analysis of the global lithium resources assumed a rapid and widespread

Table 8. Estimated lithium resources.

Source: U.S. Geological Survey, Mineral Commodity Summaries, January 2018

	Resources (Mt)
U.S.	6.8
Argentina	9.8
Bolivia	9
Chile	8.4
China	7
Australia	5
Canada	1.9
Congo	1
Russia	1
Serbia	1
Czechia	0.84
Zimbabwe	0.5
Spain	0.4
Mali	0.2
Brazil	0.18
Mexico	0.18
Portugal	0.1
Austria	0.05
TOTAL	53.35

Part 2: Concerns surrounding energy storage technologies

adoption of electric vehicles. The use of lithium-ion batteries for storage in a fully renewable economy is not considered. The time period they considered was from 2010 to 2100.

Their study was divided in three main categories: nonbattery lithium demand, batteries for portable electronics, and batteries for vehicles. Nonbattery lithium demand was estimated at 3.16 Mt for the period 2010-2100. Growth estimates from Yaksic and Tilton [105] and current demand were used. The authors underline the possibilities of substitution of lithium by other materials in these applications. In the case of portable electronics batteries, data from primary and secondary batteries was obtained, and a linear regression was done with the gross domestic product (GDP). Correlations of 95% and 99% were found for primary and secondary batteries, respectively. The estimation of global demand for batteries in the time period studied was based on (1) the regression results and (2) the growth scenarios for future GDP provided by the Intergovernmental Panel on Climate Change(IPCC) [106]. Growth scenarios of 2% and 3% were studied, the batteries were considered to have 1 year of useful life, and a 5% recycling rate was accepted, based on data from the UK and Canada. The lithium recovery of the recycled batteries was considered to be 90%. The mass of lithium used per battery was based on the following data: (1) all battery-related lithium use in 2008 was for primary and secondary batteries, (2) Sociedad Química y Minera (SQM) estimation on global lithium consumption in 2008 was 17,400 t, 27% of which was for batteries [107], and (3) Frost & Sullivan world total count of primary and secondary batteries was 4,386 million units [108]. The calculated average mass was 1.07 t Li per million batteries. It was assumed that the ratio remained constant in the studied period.

The last category concerned vehicle batteries. The demand values that were calculated are considered as upper-limits due to emerging alternative technologies (i.e. fuel cells and ultra-capacitor batteries) that could substitute vehicle batteries in the future. The estimation was done in the following manner. First, a linear regression analysis was done using light-duty global vehicle production for the period 1995-2008 from the Ward's 2009 Automotive Yearbook [109] and global GDP data. A correlation of 97% was found. Vehicle manufacturing growth was estimated following 2% and 3% GDP growth scenarios. Credit Suisse's projection of electric vehicle penetration [110] was used and beyond 2030 it was assumed that in the 2% scenario, the yearly electric vehicle growth became constant, while in the 3% scenario the industry experimented a 0.5% growth every ten years. With these assumptions, a complete penetration of the electric vehicle was found for 2083 in the 2% scenario, and for 2087 in the 3% scenario. The number of batteries needed was calculated by assuming that one car had 10 years of useful life; to calculate the lithium content of each battery, a specific electric range was assumed for each type of car (HEV, PHEV, BEV), and the battery was made bigger according to a set buffer to allow for adequate cycle life and avoid deep discharge. The authors consider that battery recycling may be a critical factor in the future. Estimates from different sources were used: lead-acid batteries used in cars are nearly all recycled (US EPA: nearly 90% [111]; International Lead Management Center: 96% in many countries [112]; International Lead Association: current 100% or possibility of 100% [113]). Based on this, the total lithium demand and recycling volumes for three recycling participation rates (90%, 96%, and 100%), with 90% lithium recovery were calculated [114].

The upper limit for total lithium demand forecast in the period 2010-2100 was calculated by the addition of the mined mass of nonbattery, portable electronic batteries, and vehicle batteries. The result was 19.6 Mt, so the upper limit was set at 20 Mt. The estimated lithium resource is quantified as 39 Mt, with an expected recovery of lithium of 19 Mt. A probable issue to be faced is that there may not be enough lithium

production operating facilities to match the demand rate. The authors of the study conclude that «Li availability will not constrain the electrification of the automobile during the present century» [104].

Another study was made by Martin et al. in 2017 [115]. It was stated that the theoretical static range of lithium was 435 years. The global production of lithium was about 40,000 t in 1995, increasing to 140,000 t in 2008. There was a significant quantitative decrease due to the economic crisis in 2009, followed by a 70% increase in the following five years. The reserves of lithium are considered large and are exploited at low cost, a fact that has the consequence that less than 1% of the metal is currently recycled [116]. Lithium recycling may be relevant from 2030, and it is forecasted to substitute up to 25% of lithium supply by 2050 [117]. Current processes aimed at battery recycling focus on cobalt and nickel recovery. The pyrolytic VAL'EAS process by Umicore NV/SA, in Belgium, and the low-temperature separation by TOXCO Inc. in the USA are examples of it [118] [119]. However, there are some companies that are shedding light on lithium recycling. One example would be a battery recycling company in Germany called Accurec Recycling GmbH (Mülheim an der Ruhr). They recycle 4,000 t/yr of spent batteries and obtain lithium carbonate (Li_2CO_3) and high-priced metals by means of a process that combines pyrolytic and hydrometallurgical techniques [120]. Other companies would be AEA Technology Group plc (Harwell, UK), Batrec Industrie AG (Wimmis, Switzerland) and Recupyl S.A.S. (Domène, France). Other processes are being studied and may be economically viable [121] [122]. Intensified recycling activities may be critical for securing long-term supply of lithium. The study considered that the major players in future lithium demand would be primary and secondary batteries (6-12%/yr) and ceramics and glasses (8-10%/yr); electric vehicles would require an additional 70,000 t of lithium carbonate equivalent (LCE) up to 2020. In 2015, 173,000 t LCE were consumed. In the “basic” scenario (growth 6%/yr), it was calculated that 230,000 t LCE would be consumed by 2020; the “optimistic” scenario (growth 9%/yr) gave a consumption of 270,000 t LCE by the very same year. Extraction projects are up and running and should meet the estimated requested demand. The authors underline that there are a number of facts that should be taken into account when estimating the quantity of lithium that is going to be needed in the future: (1) lithium recycling have had no significant impact on total supply so far; (2) lithium deposits are concentrated in a small number of countries; (3) the price of lithium carbonate has raised since 2010, and it is expected to continue doing so in the future; and (4) battery market depends on political decisions, raw materials and new battery technologies, factors which make it difficult to give a reliable forecast beyond 2020 [115].

2.4.2. Cobalt

Cobalt is used in metal alloys, batteries, electroplating, samarium-cobalt magnets, and blue pigments. This metal is typically found in copper or nickel ores. 40% of cobalt comes from the Democratic Republic of the Congo [100].

USGS estimates world terrestrial cobalt resources to be about 25 Mt, the majority of it located in Congo and Zambia, nickel-bearing laterite deposits in Australia and nearby island countries and Cuba; magmatic nickel-copper sulfide deposits hosted in volcanic rocks in Australia, Canada, Russia, and the United States. More than 120 Mt of cobalt resources have been identified in manganese nodules and crusts on the floor of the Atlantic, Indian and Pacific Oceans [123]; these resources can be located at water depths as great as 6 km, and their exploitation has been so far prevented because of technological, economic and legal barriers [124].

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Among the improvements that ought to be done regarding cobalt extraction are (1) better geologic models for cobalt-rich ores, which would allow for the exploration of new deposits; (2) improved methods to boost cobalt extraction from nickel-cobalt laterites; (3) development of processes to be able to execute an efficient and fair-priced recovery of cobalt from silicate minerals; (4) technological advances to help make mining and extraction of cobalt from deep-sea ferromanganese nodules and crusts economically viable [124].

Nearly 75% of cobalt is consumed in battery production [123], the main

consumer being China. This high demand of cobalt is one reason for the skepticism towards the widespread use of lithium-ion batteries in electric vehicles [125]: cobalt should be considered as a primary constraint for the battery market as well. The demand for cobalt is expected to grow by 70% until 2020: it is supposed to increase to 110,000 t/yr in 2030 and 190,000 t/yr in 2050 [115]. The global reserves of cobalt are about 7.1 Mt, 3.4 Mt of which are located in the Democratic Republic of the Congo, and 1.1 Mt in Australia [123]. Even though forecasts show no shortage in supply until 2050 if the supply situation in Africa remains stable [126], a shortage in cobalt supply may impact negatively on lithium demand [115]. Such a shortage happened in the late 70s, when a shortage associated with the Shaba crisis in Zaire (today the Democratic Republic of the Congo), which was the world's largest cobalt supplier, made the prices climb and prevented the industry from using the raw material anymore [127].

2.4.3. Calculations

In the Part 1 of this thesis the necessary amount of energy needed for a 100% renewable economy was calculated. Knowing the energy density of the battery and the composition of it, the required amount of resources can be easily calculated.

It was calculated that a total storage of 19,981 TWh was needed in order to provide the grid with enough energy using only renewable sources. The detail for the amounts calculated for each of the continents, along with the total worldwide results can be observed in Table 10. Currently, the energy density of lithium-ion batteries is about 150 Wh/kg [68] [69]. After consulting a few references, the estimated amounts of certain metals in a battery were calculated in a previous section: lithium accounted for 2.36% of the weight of the battery, and cobalt accounted for 19.38% of it. Therefore, building the calculated amount of storage would require 3,144 Mt of lithium and 25,815 Mt of cobalt. The total weight of the batteries would be 133,205 Mt. Lithium and cobalt reserves are estimated to be about 53 Mt and 145 Mt, respectively. The resources are then clearly not enough, and these required amounts of resources would be for only the first set of batteries, which would have eventually to be replaced. Therefore, power-to-gas should be considered as a much better alternative for energy storage in a 100% renewable-fueled economy.

Additionally, the resources needed for each of the calculated yearly scenarios in the areas that were studied were calculated. The results can be found in Table 11. The amounts required to build these batteries

Table 9. Estimated cobalt reserves.

Source: U.S. Geological Survey, Mineral Commodity Summaries, January 2018

	Reserves (Mt)
U.S.	0.023
Australia	1.2
Canada	0.25
Congo (Kinshasa)	3.5
Cuba	0.5
Madagascar	0.15
New Guinea	0.051
Philippines	0.28
Russia	0.25
South Africa	0.029
Zambia	0.27
Others	0.56
TOTAL	7.1

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are obviously smaller, even some of them could not be built because of insufficient resources. On the other hand, these results may suggest that using batteries for energy storage in small remote communities may be a viable solution. Economic factors will determine whether batteries or other forms of energy storage would be a better fit for the case. In a general case, the resources that are currently needed to build a battery for an entire country or large region are, to date, clearly not enough. With the development of new materials, this might become a plausible solution in the future.

The reader must not forget that the calculated storage amounts are assuming a hundred percent roundtrip efficiency, so the efficiency factor should be applied when necessary, according to the battery at use. The battery then will always be bigger, which is to say, that the amounts of resources needed to manufacture it will be even larger.

Information

- Lithium resources: 53 Mt
- Cobalt resources: 145 Mt

Table 10. Battery mass and lithium and cobalt mass requirements for each of the scenarios calculated for each continent, the sum representing the total worldwide amount. Storage based on the yearly results.

	Storage (TWh)	Battery mass (Mt)	Lithium mass (Mt)	Cobalt mass (Mt)
<i>Africa</i>	1.088	7,250.82	171.12	1,405.21
<i>America</i>	4,919	32,794.12	773.94	6,355.50
<i>Asia</i>	10,178	67,850.08	1,601.26	13,149.35
<i>Europe</i>	3,592	23,946.56	565.14	4,640.84
<i>Oceania</i>	205	1,363.45	32.18	264.24
TOTAL	19,981	133,205.02	3,143.64	25,815.13

Table 11. Battery mass and lithium and cobalt mass requirements for each of the scenarios calculated for Germany, Austria and Luxemburg, and California, respectively. Storage based on the yearly results.

		Storage (TWh)	Battery mass (Mt)	Lithium mass (Mt)	Cobalt mass (Mt)
Germany, Austria and Luxemburg	#11a	55.65	371.01	8.76	71.90
	#12a	110.55	737.05	17.39	142.84
	#13a	78.46	523.06	12.34	101.37
	#14a	285.34	1902.24	44.89	368.65
	#15a	184.28	1228.52	22.99	238.09
California	#11b	23.23	154.89	3.66	30.02
	#12b	25.64	170.92	4.03	33.12
	#13b	23.14	154.27	3.64	29.90
	#14b	22.71	151.39	3.57	29.34
	#15b	22.14	147.60	3.48	28.60

2.5. Challenges

According to Whittingham, Professor at the State University of New York at Binghamton, an expert in the field of battery development and one of the people who developed Exxon's rechargeable lithium battery,

the list of challenges that battery scientists need to overcome is remarkably long: cheaper materials, good electrolytes, improved separators (new materials), better geometries for cells... [10 págs. 192-193].

Battery technology is regarded as rather slow-developing. Its cell potential, capacity, and energy density, which are used to analyze its performance, are directly related to the materials that form their electrodes. Interfaces between electrodes and electrolytes determine their lifetimes, while safety depends on the stability of the electrode materials and interfaces. Rechargeable lithium-based batteries are considered to be in their early phase of development, and the hope is placed on solid-state chemistry. One complication is that the characteristics that are going to be needed are unknown, but different necessities mean using different materials for both the electrodes and the electrolyte [2].

New materials are being investigated to replace the ones being used today in the electrodes, as seen in a previous section. For instance, a high capacity anode based on nanostructured silicon with a theoretical-specific capacity of 4200 mAh/g is being studied [128] [129] [130]. The exploration of carbon and silicon composites obtained from pyrolysis of silicon-containing polymers is also being carried out for anode materials [131] [132] [133] [134]. In general, nanomaterials are attracting a lot of attention. The electrochemical properties of this type of materials are both size and shape dependent. One of its main drawbacks is that their volumetric energy is generally rather low due to their low density (e.g. $\rho_{\text{graphene}} = 0.03 \text{ kg/L}$, $\rho_{\text{graphite}} = 1.3 \text{ kg/L}$). Deng suggests using microstructures based on nanomaterials to increase the density of the materials while maintaining nanomaterials' desirable properties, instead of using materials with random nanoparticles [4].

Currently-used cathode materials compromise cell capacity. LiCoO_2 is expensive and highly toxic, and emerging LiFePO_4 has a low capacity. Ni-Co-Mn-based cathodes may be a solution, even though their capacity is considered moderate, and both nickel and cobalt are expensive and toxic. Most likely, future cathodes will be manganese or iron based, and the conductivity issue will be addressed by means of nanotechnology [4].

Other battery technologies being developed for various applications include sodium-ion, magnesium-ion, calcium-ion, aluminum-ion, fluoride-ion, lithium-air (lithium-oxygen), and lithium-sulfur [4].

Energy density of batteries should also be increased: it is desirable to find electrode couples with both high-specific capacities and high operating cell voltage. Silicon and tin based anodes are considered attractive, as previously explained, but the capacity of manufacturing nanomaterials at a large scale with a reasonable cost is nowadays still an issue. One of the future anodes could be a tin and silicon based composite [135].

Safety issues need to be addressed, as there have recently been accidents because batteries caught on fire. This has happened in the Boeing 787 passenger aircrafts and Tesla Model S cars. Environmental issues are also a concern, and future batteries should use biologically derived organic or inorganic electrodes, paired with aqueous electrolytes [4]. Virus-assisted synthesis for electrode materials is being studied [136]. Life cycle assessment should also be considered when designing a battery; today little is known about the environmental impacts of the production, use and disposal of next-generation of lithium-ion batteries [137].

Rate performance is another current research topic, since the time consumed to charge a battery is considered excessive for its use in some applications. This time should ideally be dramatically reduced, especially for the use of batteries in the automotive industry [4] [138].

Conclusions

In this thesis a study about the energy consumption and renewable capacity of two areas, one being formed by Germany, Austria and Luxemburg, and another one being California, has been done. Based on the available data, the needed scaling factor for each renewable source in each of the locations was calculated. After applying the considered objective function on the yearly storage requirements, the region formed by Germany, Austria and Luxemburg was found to have a storage requirement of 78,459,600 MWh. The scaling factors needed in this case were 2.14 for solar and 4.42 for wind, which meant capacities of 88,700.86 MW and 232,925.16 MW, respectively, for solar and wind. In this scenario, the needed battery would weigh 523.06 Mt, which means that 12.34 Mt of lithium and 101.37 Mt of cobalt would be required to build it. The same criterion was applied to California. In this case, a storage requirement of 22,139,900 MWh was found. The needed scaling factors were 7.68 for solar and 2.67 for wind, which meant capacities of 66,186.24 MW and 15,069.48 MW, respectively, for solar and wind. In this scenario, the needed battery would weigh 147.60 Mt, which would require 3.48 Mt of lithium and 28.60 Mt of cobalt. It is important to take into account the fact that this storage refers to a 100% roundtrip efficiency of the battery. Therefore, if it were put into practice, the specific roundtrip efficiency of the battery being used should be considered.

Afterwards, the storage needed for a 100% renewable economy was calculated. The data, along with the results of the storage calculations, was used to calculate the fraction of energy that was provided by each of the renewable sources studied. With this information, an equation that could be used to calculate the storage needed for other regions in the world by having their approximate renewable potential (fraction) and consumption was found. A sensitivity analysis for the equation was done in order to determine whether the result of the equation would vary largely if the potentials were changed. It was found to have a rather low variability. This way, the estimated total energy storage for the world was calculated and found to be 19,981 TWh. This would require a battery that would weigh 133,205 Mt, and resources of 3,143.64 Mt of lithium and 25,815.13 Mt of cobalt.

An in-depth study about the currently used batteries was also done. By knowing their composition and averaged energy density, the estimations of the amount of critical metals studied in this thesis (lithium and cobalt) that are printed above and that would be needed to build the required energy storage previously found were calculated. Considering the shared amounts and knowing that the lithium and cobalt resources are estimated to be about 53 Mt and 145 Mt, respectively, it is easy to see that the amount that was found in both cases is too large to be executed. The solution may only work at small scale.

The recycling processes being used to date were observed, but most of them are only at the research stage. Most of them combined physical and chemical processes, the latter being the ones that have traditionally been used in the mine industry to extract metals (hydrometallurgy).

It was therefore determined that the use of batteries for a worldwide energy storage system is not a feasible solution. Other systems, such as power-to-gas, would undoubtedly be a better match, as they are much less resource-intensive, and they could be combined with the existing natural gas infrastructure for lowered costs. Another study by GreenTechMedia reached some conclusions that are consistent with the results obtained in this thesis [139]. They also studied the areas of California and Germany (in the present thesis the area concerning Germany also considered Austria and Luxemburg, but these are countries next to

Germany and very alike in climatological characteristics). Even though their approach was quite different, focusing more on system alternatives, technologies, and economical aspects, it was also concluded that batteries were not a good fit for large term energy storage –in this case, the reason was that the solution would be more expensive. Resources were not considered–. Additionally, they concluded that wind was a better match for the load in an hour-by-hour basis, which is consistent with the results here obtained, since the storage needed for wind only and for wind-favored calculations is smaller. In long-term storage, they favor solar in California and wind in Germany, and the calculated percentages are quite similar. They were set in California for 90% solar and 10% wind, while in the present thesis they were set for 81% and 19%. In Germany the results were even closer: they decided on 30% solar and 70% wind, and they were set here for 28% solar and 72% wind.

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