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Integration of Salt Cavern Hydrogen Storage in a 100% Renewable Energy Supply Scenario

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Abstract:

We address two critical environmental and technical problems for the integration of subsurface salt cavern hydrogen storage with 100% renewable electricity. First, the storage/production rate of hydrogen must match the unpredictable pattern of renewable electricity supply and (more predictable) demand for electricity by creating and strategically locating enough salt caverns. Secondly, creating and maintaining so many salt caverns requires large volumes of fresh/seawater. We develop two static and dynamic models for Denmark as a successful case of wind power development, considering the surplus energy and demand forecasts. The static model predicts the minimum amount of hydrogen needed for balancing the average annual supply and demand of electricity and fresh water necessary for the construction of required salt caverns. The model considers all the round-trip exergy losses of electricity-H2-electricity in the electrolyzers, fuel cells, compressors, and pipelines. The dynamic model considers the variable supply from wind farms and user demand over time; We also include the effect of the inertia of the electrolyzers, fuel cells, and compressors, and technical constraints, e.g. salt cavern pressure and pipeline flow capacity, to design sufficient storage sites that can dynamically balance the fluctuating supply of renewables and variable user demand. The static model predicts a realistic volume of salt caverns for storing the surplus green hydrogen; however, in the absence of small-scale storage solutions (batteries), we show that the number of required caverns and injection/production wells become unrealistically high, with high energy demand and cost for maintenance water treatment.

Keywords:

Salt Caverns, Energy Storage, Hydrogen Storage, Renewable Energy.

1. Introduction

The unprecedented consequences of climate change caused by greenhouse gases emissions and the geopolitical circumstances have increased investments on renewable energy production to limit the environmental impact while maintaining the energy security. The increasing penetration of intermittent renewable energy sources, i.e., wind and solar, in the energy production mix stresses the necessity of finding storage solutions to cope with their intrinsic intermittency and unpredictability. In a fully renewable scenario, it is necessary to evaluate which are the most convenient and relevant solutions for storage. Here, we address these concerns focusing on the salt cavern storage of green hydrogen integrated in the electricity supply of Denmark. Different solutions for energy storage exist (Figure 1), with different storage capacity and power rating (i.e. energy charge and discharge per unit time). Many of these technologies are already available commercially, while some others are in lower Technology Readiness Level (TRL).

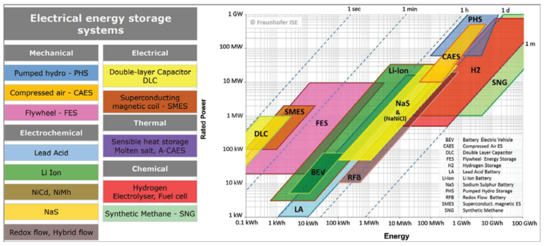

Figure 1: Classification of electrical energy storage systems according to energy form (a); Comparison of rated power, energy content and discharge time of different EES technologies (b), own representation based on (International Eletrotechnical Commission (IEC), 2011).

Electrochemical technologies cover the majority (over 85% as 2016 new installation data) of the new energy

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storage solutions, with the Li-Ion technology being the predominant one. Research and development is focused on increasing the number of charge cycles (i.e. the number of times the battery can charge and discharge), reducing production costs and tackling the recycling problem. Different technologies are available, e.g., NaS (Sodium Sulphur), $NaNiCl_2$ (Sodium Nickel Chloride), Pb-Acid (Lead-Acid), Li-Ion (Lithium Ions), Ni-MH (Nickel metal hybrid), Ni-Cd (Nickel-Cadmium), and flow batteries, all with a general common issue of not presenting sufficiently high energy densities to be considered for large storage systems. Second type of technologies is Thermal Energy Storage (TES). All TES technologies are based on the usage of thermal energy as mechanism of storing energy [5]: **MSTES** (Molten Salt thermal energy storage) is the most used TES technology; it has good heat transfer properties and relatively low cost; drawback is the usage of corrosive salts and the necessity of maintaining a minimum temperature value to avoid the solidification of the salts. **PCM** (Latent-phase change material) is based on the latent heat stored by phase change material; as TCS this technology is still in a development stage. **TCS** (Thermochemical storage) where heat or cold is stored by means of different chemical reactants; as PCM, it is in a development stage. **SHS** (Sensible Heat storage) is another possibility to store energy through sensible heat storage; this storage can be done through the usage of solid materials (like sand, concrete or similar materials [4]) or liquid materials (most common used is water, fundamental in the solar thermal systems [11]). TES technologies are mainly in development stage so they do not represent at the moment a suitable solution for our purpose. The most exploited large-scale technologies for energy storage are based on storage of energy through gravity (for hydro) and pressure (for CAES) [4] [8]. These technologies allow high long-term energy storage capacities but present major drawbacks as high investment costs (for civil constructions), high environmental impact (especially hydro), not widely available conditions for their construction and high inertia of the system (charge-discharge process) compared to electrochemical or electrical storage technologies. Electrical storage technologies, like SMES (superconduction magnetic energy storage), Capacitors and Supercapacitors, allow high power densities and really fast charge/discharge times (as well as response times) but they have low energy density so they are not useful for large-scale energy storage purposes. Here, we focus on green hydrogen that has a higher energy density compared to TES and CAES, and can be stored in much larger scales in the safe subsurface salt caverns. The technology is mature, but the current research is generally focused on the capacity and safety of storage. Consequently, the production rate that is critical to the integration of hydrogen storage in the energy networks, has not received considerable attention specially on its technical aspects. We will, therefore, focus on the dynamic behaviour of salt cavern storage and production of hydrogen in the Danish future electricity network to further investigate the technical obstacles of integrating salt caverns in a realistic safe and resilient energy supply and demand scenario.

2. Materials and Methods

The base of this project is the analysis of salt caverns hydrogen storage solutions to permit the switch to a completely renewable energy-based society. To cover the entire energy demand curve with only resources like wind or solar it is necessary to consider a storage solution that is able to cope with the intermittency and unpredictability of the renewable supply. The analysed storage solution is artificial subsurface salt caverns: the calculations have started with an estimation of the amount of hydrogen that must be produced to cover the demand. Once completed, it has been possible to calculate the required salt caverns volume that had to be artificially created.

This type of static analysis has been carried out considering initially a simplified model. In this model a limited number of cities and storage locations has been considered and their positioning and connections have been manually evaluated. This method will be explained in the dedicated section 3.1.. The consequences of the functioning of the system in terms of behaviour over time, with a set of defined assumptions, will be instead analyzed in the second dedicated paragraph 3.3.. The case study related to Danish 2050's wind production and demand projections starts with the simplified model case.

3. Case Study

3.1. Simplified Model

In order to proceed in the study and evaluation of the simplified model it has been necessary to make few assumptions:

1. No limits on number and dimension of wind farms that can be installed in the North Sea: this hypothesis doesn't differ excessively from the actual conditions present in the North Sea.
2. Analysis starts from the demand and goes backwards, considering all the efficiencies of the components of the energy system, to the necessary production to cover it.
3. Electrolyzers are considered to be modular so the efficiency is evaluated as approximately independent from the size of the plant.

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4. It is considered possible to place caverns for storage on the entire area of the simplified map (even though some more limited regions are considered to proceed with the modelling process).
5. All industries have been able to convert their production lines and processes to the usage of hydrogen instead of methane: this hypothesis is used to pursue the simplified analysis but the conversion of the industrial lines to hydrogen could be an issue that has to be addressed.
6. Injection and extraction points are considered placed in the center of the respective regions and it is supposed to have one cavern for each city of the model.

Before defining all the scenarios it is necessary to design a simplified map for the calculations (sm stands for simplified map), which is here reported (Figure 2).

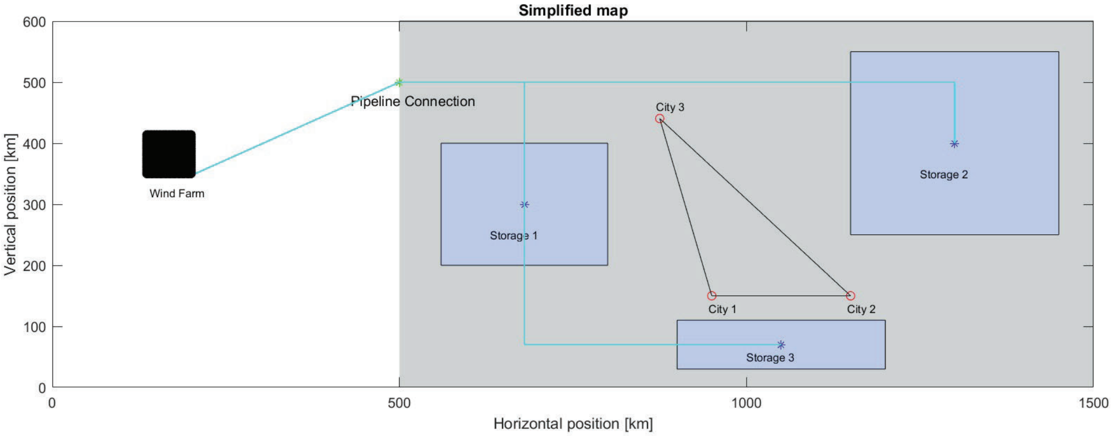


Figure 2: Map for the simplified model with pipeline connections

In this map three cities have been reported, considering a subdivision of the peak power requested into 50%, 30% and 20% respectively for cities 2, 3 and 1. The storage sites 1, 2 and 3 are respectively dedicated to cities 3, 2 and 1. Under the hypothesis of having in 30 years four times the wind power capacity and 1.5 times the power demand by users, through the Danish data of the last 10 years the future trends of production and consumption have been evaluated for each city (Figure 3) and overall (Figure 4).

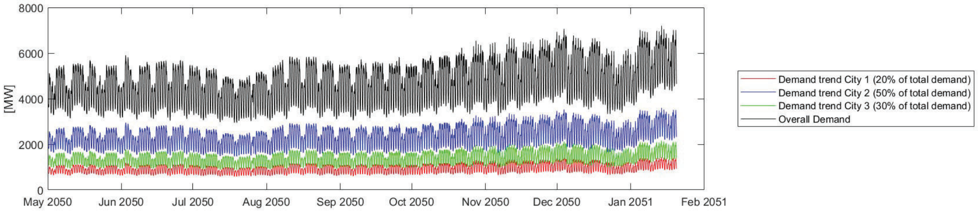


Figure 3: Projection of demand trend for each city and overall in 30 years based on Danish past electricity supply and demand data

We have assumed one offshore wind farm that covers all the electricity production. Moreover, we have defined a hydrogen island where we have the convergence of the power produced by the wind farm, the electrical transformers and the hydrogen production and storage. It is important to note two characteristics of this island:

- Average Sea Depth: North Sea has an average depth of 90 m with maximum depth of 700 m so it has been considered a value of 200 m for the analysis. [1]
- From the 20 GW 70% H_2 case (page 51 of [12]) we have obtained a set of reference dimensions for the artificial island.

With a temporal resolution of 1 hour, a 9-months time frame considered and an overall shortage (calculated as the difference between the overall demand and the wind farm production per each unit of time) in terms

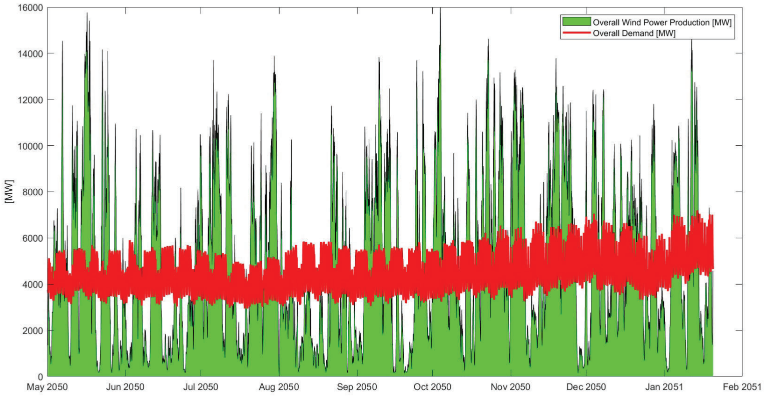


Figure 4: Projection of overall demand and wind production trend in 30 years based on Denmark's supply and demand data in 2020

of power it has been possible to integrate over time to obtain the energy shortage and divide per each city obtaining:

- $E_{shortage,city1} = 6.97 \times 10^4$ MWh
- $E_{shortage,city2} = 1.74 \times 10^5$ MWh
- $E_{shortage,city3} = 1.05 \times 10^5$ MWh

We then calculate the surplus that has to be extracted and stored to cover these shortages.

3.2. Analysis and Results

3.2.1. Fraction of surplus energy needed

With the efficiency ranges of fuel cells and electrolyzers (see Table 1 and Table 2), we calculate and obtain the energy required surplus to cover the average shortages, presented in this paragraph. The conversion efficiency to hydrogen and back to electricity are considered in our calculations.

Table 1: Overview of main electrolyzers technologies efficiencies [13]

Technologies	**Minimum Efficiency [%]**	**Maximum Efficiency [%]**
Alkaline	51	65.3
PEM	55.5	72.4

Table 2: Overview of main Fuel Cells technologies efficiencies [3]

Technologies	**Electrolyte**	$T_{operating,min}[K]$	$T_{operating,max}[K]$	$\eta_{electrical,min}[\%]$	$\eta_{electrical,max}[\%]$
AFC	Aq. KOH	333.15	393.15	60	60
DMFC	PEM	303.15	363.15	80	80
MCFC	Molten Li2CO3 and K2CO3	873.15	923.15	45	47
PAFC	Phosphoric Acid	433.15	473.15	40	40
PEMFC	PEM	333.15	363.15	53	58
SOFC	Yttrium stabilized zirconia	1073.15	1273.15	35	43

Considering these efficiencies permits to understand the amount of energy that has to be taken from the surplus to cover this shortage of electricity and quantify the energy losses. The quantities for all cities are reported in Table 3, while a bar chart has been used to evaluate the requirements for each city based on the electrolyzers-FC technologies considered (Figure 5). These values may change quite significantly with the chosen conversion technology, from average values in the order of $10^5 MWh$ for maximum efficiency factors to values in the order of $10^6 MWh$ for the minimum efficiency factors.

Table 3: Average energy [MWh] that has to be used from surplus to cover the shortage for all cities considering the minimum and maximum efficiencies for each fuel cell technology (columns) and electrolyzers (rows)

	AMC		**DMFC**		**MCFC**		**PAFC**		**PEMFC**		**SOFC**	
Alkaline	$1.14*10^6$	$8.90*10^4$	$8.55*10^4$	$6.68*10^4$	$1.52*10^6$	$1.13*10^6$	$1.71*10^6$	$1.34*10^6$	$1.29*10^6$	$9.21*10^4$	$1.95*10^6$	$1.24*10^6$
PEM	$1.05*10^6$	$8.03*10^4$	$7.85*10^4$	$6.02*10^4$	$1.40*10^6$	$1.03*10^6$	$1.57*10^6$	$1.20*10^6$	$1.19*10^6$	$8.30*10^4$	$1.80*10^6$	$1.12*10^6$

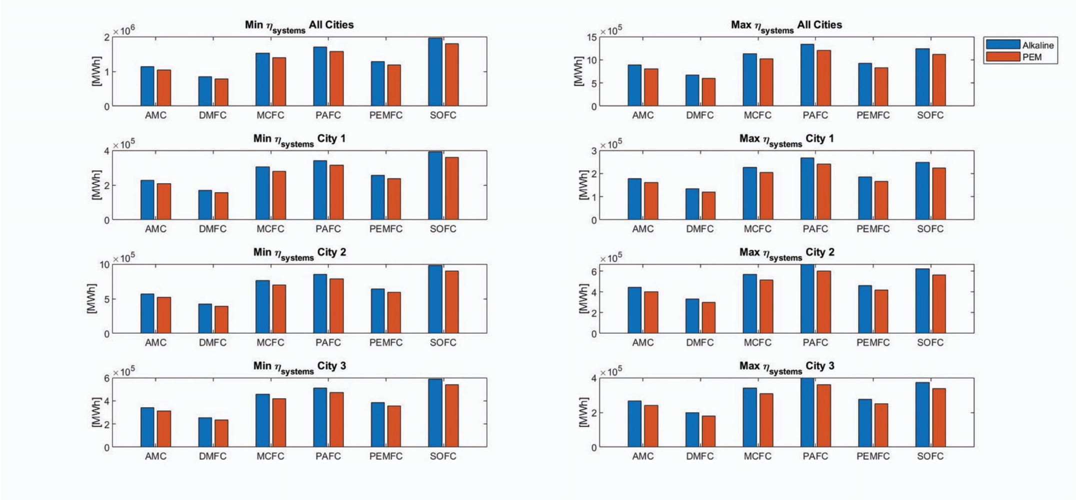


Figure 5: Visual representation of energy requirements from surplus considering minimum and maximum efficiencies of each system for all the cities and for each city taken singularly

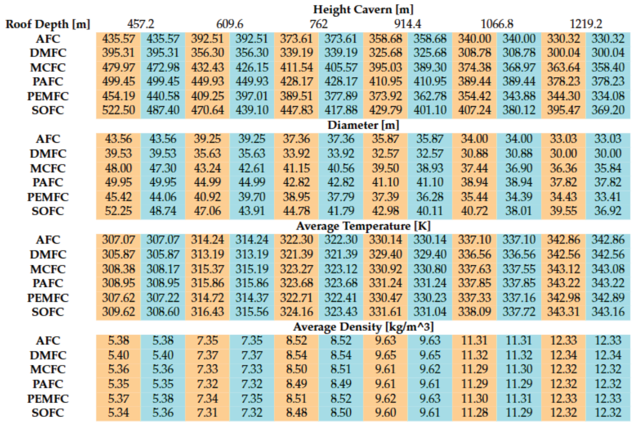
After estimating the energy that has to be stored and the fraction of energy surplus that has to used to address the energy shortage, we define two scenarios. The first one is based on production of hydrogen in a dedicated offshore island and then sent to the coast to the storage sites. The second possibility is energy transmission through electrical cables, meaning that hydrogen storage and conversion is done offshore and the onshore storage is done with hydrogen produced locally.

3.2.2. Evaluated Scenarios: Hydrogen Island and local production

In this scenario it is considered that hydrogen is produced and transmitted to onshore storage sites through the usage of pipelines. In both this scenario and the following electrical one there is the presence of offshore storage site, used as first storage location. This storage site can be considered as a solution also to avoid the construction of onshore storage sites but the costs for the construction are higher offshore than onshore. Considering the presence of an offshore wind farm at a distance of 300 km from the coast in east direction, we evaluate: the production and storage of hydrogen offshore, the transmission of it through pipeline, and the conversion to electricity onshore through the usage of fuel cells. Previously (3.2.1.) the calculations of the energy shortages and the storage (energy and hydrogen) have been presented. Now we also include the energy required for the compression for storage, the compression for transmission and the volume of the necessary artificial salt caverns. The production of hydrogen is carried out in a designated artificial hydrogen island which should be placed at maximum 5 km from the wind farm. Moreover, its position has to be chosen considering aspects like the positioning of salt caverns and the pipeline design, as presented in Figure 2.

To evaluate the dimensions of the necessary salt caverns and, at the same time, the effect on hydrogen density and the geothermal gradient, we developed an iterative function. This permitted to calculate the dimensions (height and diameter), average temperature and average density starting from the the cavern roof depth, an initial estimate of the cavern bottom depth, storage pressure, mass of hydrogen to be stored, an equation of state for hydrogen density, and the height-diameter ratio of the cavern. The cavern roof depth and the pressure, considered to be the maximum pressure, have been taken from the set of values (cavern roof depth, maximum and minimum storage pressures) cited in [9]. The results for the first city, in terms of height and diameter of the caverns, are reported in Table 6.

In order to evaluate the amount of freshwater needed to build the salt cavern the construction process of the horizontal caverns HA-4 and HA-5 in Huai”an (China) has been taken as reference [6]. For these caverns the



Roof Depth [m]	457.2		609.6		762		914.4		1066.8		1219.2	
Height Cavern [m]												
AFC	435.57	435.57	392.51	392.51	373.61	373.61	358.68	358.68	340.00	340.00	330.32	330.32
DMFC	395.31	395.31	356.30	356.30	339.19	339.19	325.68	325.68	308.78	308.78	300.04	300.04
MCFC	479.97	472.98	432.43	426.15	411.54	405.57	395.03	389.30	374.38	368.97	363.64	358.40
PAFC	499.45	499.45	449.93	449.93	428.17	428.17	410.95	410.95	389.44	389.44	378.23	378.23
PEMFC	454.19	440.58	409.25	397.01	389.51	377.89	373.92	362.78	354.42	343.88	344.30	334.08
SOFC	522.50	487.40	470.64	439.10	447.83	417.88	429.79	401.10	407.24	380.12	395.47	369.20
Diameter [m]												
AFC	43.56	43.56	39.25	39.25	37.36	37.36	35.87	35.87	34.00	34.00	33.03	33.03
DMFC	39.53	39.53	35.63	35.63	33.92	33.92	32.57	32.57	30.88	30.88	30.00	30.00
MCFC	48.00	47.30	43.24	42.61	41.15	40.56	39.50	38.93	37.44	36.90	36.36	35.84
PAFC	49.95	49.95	44.99	44.99	42.82	42.82	41.10	41.10	38.94	38.94	37.82	37.82
PEMFC	45.42	44.06	40.92	39.70	38.95	37.79	37.39	36.28	35.44	34.39	34.43	33.41
SOFC	52.25	48.74	47.06	43.91	44.78	41.79	42.98	40.11	40.72	38.01	39.55	36.92
Average Temperature [K]												
AFC	307.07	307.07	314.24	314.24	322.30	322.30	330.14	330.14	337.10	337.10	342.86	342.86
DMFC	305.87	305.87	313.19	313.19	321.39	321.39	329.40	329.40	336.56	336.56	342.56	342.56
MCFC	308.38	308.17	315.37	315.19	323.27	323.12	330.92	330.80	337.63	337.55	343.12	343.08
PAFC	308.95	308.95	315.86	315.86	323.68	323.68	331.24	331.24	337.85	337.85	343.22	343.22
PEMFC	307.62	307.22	314.72	314.37	322.71	322.41	330.47	330.23	337.33	337.16	342.98	342.89
SOFC	309.62	308.60	316.43	315.56	324.16	323.43	331.61	331.04	338.09	337.72	343.31	343.16
Average Density [kg/m^3]												
AFC	5.38	5.38	7.35	7.35	8.52	8.52	9.63	9.63	11.31	11.31	12.33	12.33
DMFC	5.40	5.40	7.37	7.37	8.54	8.54	9.65	9.65	11.32	11.32	12.34	12.34
MCFC	5.36	5.36	7.33	7.33	8.50	8.51	9.61	9.62	11.29	11.30	12.32	12.32
PAFC	5.35	5.35	7.32	7.32	8.49	8.49	9.61	9.61	11.29	11.29	12.32	12.32
PEMFC	5.37	5.38	7.34	7.35	8.51	8.52	9.62	9.63	11.30	11.31	12.33	12.33
SOFC	5.34	5.36	7.31	7.32	8.48	8.50	9.60	9.61	11.28	11.29	12.32	12.32

Figure 6: Results for city 1 in terms of Height and Diameter of caverns, average temperature and density of hydrogen; the orange colour refers to the minimum efficiency of FC technologies, the light blue refers to the maximum

characteristics are presented in the Table 4.

Table 4: HA-4 and HA-5 cavern and building process characteristics (Huai"an, China) [6]

Cavern	**HA-4**	**HA-5**
Volume Cavern [m^3]	52000	121000
Volume Freshwater Needed [m^3]	3329000	3690000
Volume Cavern/Volume Freshwater needed	64.02	30.50
Concentration Brine [kg_{salt}/m^3]	300	

From the volume ratio of cavern to freshwater needed for salt cavern construction, we calculated the volume of freshwater needed considering the minimum and the maximum values of this ratio and the minimum and maximum efficiencies of the FC technologies. The amount of freshwater needed in all cases (maximum and minimum efficiency for FC technologies, maximum and minimum volume ratio cavern - volume freshwater) is not negligible and has to be taken into account in terms of environmental impact and economic costs to treat and transport the salty brine after dissolving the subsurface salt. Lastly, it has been evaluated the pressure drops of the hydrogen pipelines necessary to cover the energy demand for each city. Based on a defined set of assumptions the pressure drops have been calculated and presented in Table 5. The values of the pressure drops make necessary the presence of intermediate pumping stations to increase the pressure and guarantee the arrival of the hydrogen to the storage sites.

Table 5: Pressure drops in [*bar*] per each pipeline (column, first for city 1, second for city 2 and third for city 3), considering all the FC technologies (rows) with their minimum and maximum values of efficiencies

	Min η_{FC}			**Max η_{FC}**		
AFC	305.00	282.74	759.39	234.07	295.03	654.65
DMFC	375.93	442.55	903.41	361.74	381.08	890.32
MCFC	191.51	221.27	536.81	241.16	270.44	602.28
PAFC	156.04	245.86	549.90	156.04	233.57	445.16
PEMFC	255.35	282.74	680.83	198.60	295.03	615.37
SOFC	163.14	233.57	405.88	177.32	295.03	628.46

The second possible solution is the transmission of energy through the usage of electrical lines and having the production of hydrogen directly on the storage sites. In this scenario there is no hydrogen transmission through pipelines: hydrogen is produced on the hydrogen island and stored offshore in a dedicated site for the purpose of converting to electricity when the windmills are down. Hydrogen is also produced onshore with surplus of energy sent with electrical interconnection between the hydrogen island and the shore. The possible presence of offshore storage would permit to reduce the number of storage sites onshore and to increase the social acceptance of the hydrogen storage on the first place. As for the other scenario, the analysis has been carried out from the storage site while acknowledging that it is necessary to consider also the efficiency of electrical

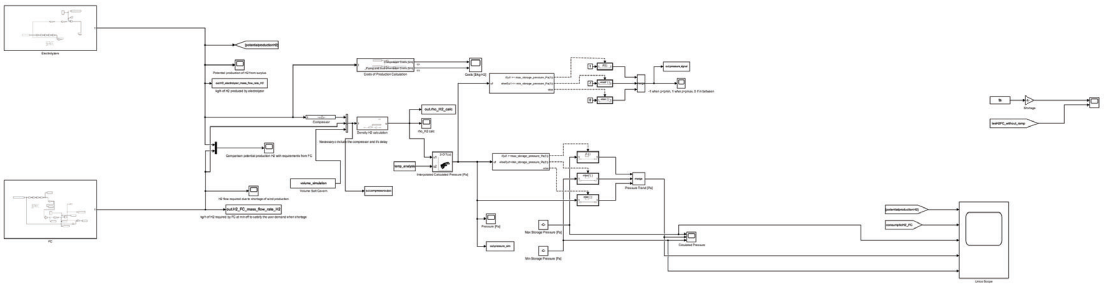


Figure 7: Simulink Dynamic Model

transmission from sites to cities.

The process for the calculation of the dimensions of the artificial caverns is the same as the previous scenario, the main difference is related to the addition of electrical components (with their efficiencies) between the hydrogen island and the onshore storage sites. The elements that have to be considered are inverters (DC-AC), transformers (AC-AC) and transmission lines (in DC or AC).

3.3. Dynamic Model

In section 3.1., the hydrogen storage requirements have been analyzed and calculated considering a static approach, serving two purposes: first, the overall shortage of energy caused by the mismatch of the wind production and the user demand curves. Secondly the percentage of the surplus needed to cover that shortage through the production and storage of hydrogen. The latter point has been carried out taking into account constant values of the efficiencies of the components of the system and ignoring the dynamic behaviour of the system. Here, we consider the functioning and the consequences of the behaviour of the system components over time, under a defined set of assumptions, that includes:

1. The system is considered to be isolated thus no interconnections with other countries or grids are considered.
2. We projected the increase of the wind power installed and the increase of user demand with an expected enhancement of 50% of the current demand and a nominal wind power installed equal to 5 times the currently installed power with respect to the data considered (2017-2019).
3. Dynamic behaviour for electrolyzers, fuel cells (start up and ramp up time) and compressors (time to reach predefined pressure specifications) are considered.
4. The model used for the description of the storage behaviour is 0-D (zero-dimensional or bulk model).

a Matlab script and a Simulink model have been developed to calculate the impact of inertia of system components and the constrained injected and extracted mass flow rates and fixed volumes of storage sites on the security of energy supply for a dynamic demand. We also use the script to estimate the required number of caverns for a balanced supply and demand of electricity in Denmark.

Figure 7 shows the Simulink model developed to solve this problem, implementing specific subsystems (with relative control systems) for fuel cells, electrolyzers and compressors necessary to manage the system and allowing it to be able to follow the demand and production trends (Figure 8). Here the electrolyzers system (with its control system) is briefly presented. For the fuel cell system the function principle is similar.

3.4. Electrolyzers system

Electrolyzers functioning (as molar flow rate of hydrogen produced [mol/s]) is related, following the Faraday's law (Equation 1), to the number of cells n_{cells}, to the current flowing through I_{Ez}, Faraday's parameter F, and Faraday's efficiency η_F (calculated with Equation 2). [10]

$$\dot{n}_{H_2} = \frac{n_c I_{Ez}}{2F}\eta_F \tag{1}$$

$$\eta_F = 96.5 \exp\left(\frac{0.09}{I_{Ez}} - \frac{75.5}{I_{Ez}^2}\right) \tag{2}$$

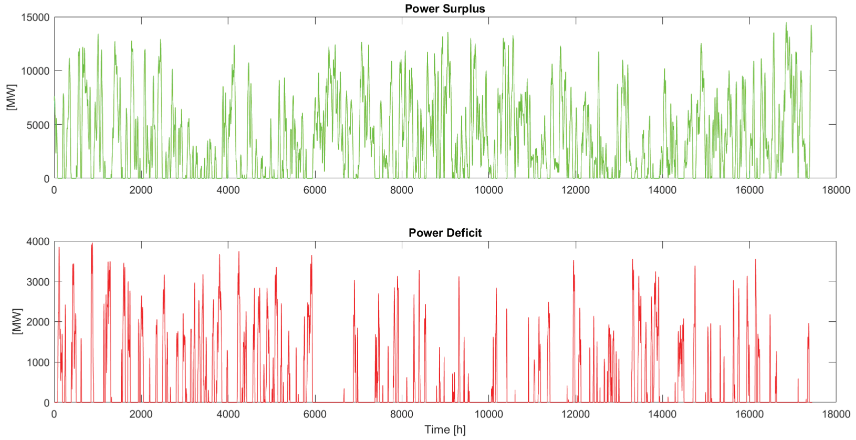


Figure 8: Power surplus and deficit of the system (expressed in [MW])

In the analysis, a simplified version of electrolizer efficiency is considered, that is independent of the above parameters and the outlet pressure. Instead, we consider the behaviour over time of the electrolyzers in terms of start-up time (supposing a hot start-up) and ramp-up time, which are respectively defined as the time interval between the electrical connection and the beginning of the hydrogen production and the time interval necessary to reach the nominal power output from the end of start-up process.
These two parameters have been considered as part of the main simulation and have been obtained from data of products available on the market, like the electrolyzer Plug EX-425D [2]. They have been fixed at these values (even though they have been modified to see their impact on the simulation):

- $\Delta t_{Start-Up} = 10s$
- $\Delta t_{Ramp-Up} = 30s$

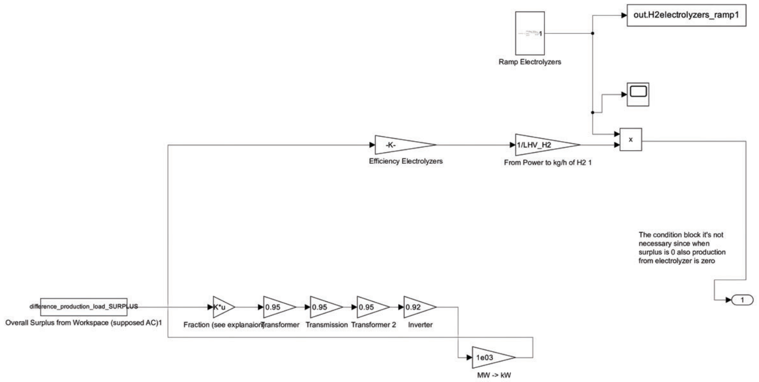


Figure 9: Simulink electrolyzer simplified model

These parameters have been added to Simulink as presented in Figure 9. It has been considered a constant value of efficiency and then converted the value of energy consumed by electrolyzers to the amount of hydrogen produced. Considering the start-up and ramp-up times, we obtain the produced hydrogen mass flow rate over time (Figure 10). This mass flow rate has been then used in the zero-dimensional storage model to evaluate the amount of hydrogen stored and withdrawn over time. It is important to highlight that not the entire overproduction is converted into hydrogen to reduce the number of electrolyzers required. For this purpose a value of 30% of the surplus production has been considered and also varied to evaluate the impact of this parameter on the system.

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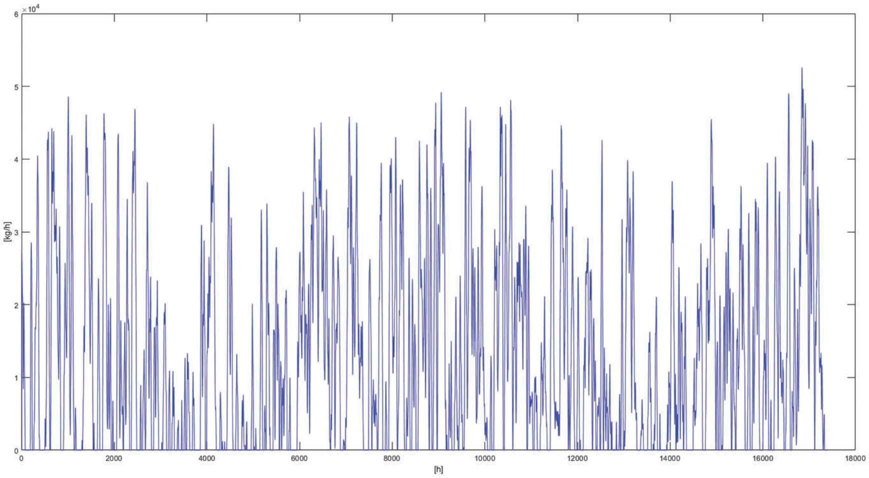

Figure 10: Electrolyzers hydrogen mass flow production rate (reference conditions)

3.5. Parameters of the simulation

The following parameters are the reference ones of the simulation :

- $fraction_{surplus} = 0.3 \Rightarrow$ fraction of the wind surplus power that is used to power the electrolyzers;
- $percentage_{fillingstorage} = 0.8 \Rightarrow$ initial percentage of storage filling;
- $T_{H_2} = 300K \Rightarrow$ fixed temperature for the analysis;
- $\Delta t_{Start-up,El} = 10s \Rightarrow$ start-up time for electrolyzers;
- $\Delta t_{Ramp-up,El} = 30s \Rightarrow$ ramp-up time for electrolyzers;
- $\Delta t_{Start-up,FC} = 10s \Rightarrow$ start-up time for FC;
- $\Delta t_{Ramp-up,FC} = 15min = 900s \Rightarrow$ ramp-up time for FC;
- $V_{simulation,firstattempt} = 6.49 \times 10^8 m^3 \Rightarrow$ first attempt value for simulation storage volume (placed equal to the volume of storage in first case of minimum efficiency in the static model multiplied by 10^3);
- $\Delta p_{\%,Max,FC} = 10\% \Rightarrow$ maximum percentage pressure drop admitted for storage-FC pipelines;
- $d_{pipe,FC} = 18cm = 0.18m \Rightarrow$ diameter extraction well and storage-FC pipeline connection (considered a typical value for natural gas underground storage wells diameter [7])
- $\Delta p_{\%,Max,El} = 5\% \Rightarrow$ maximum percentage pressure drop admitted for electrolyzers-storage pipelines;

the simulation has returned the results presented in Table 6:

Table 6: Simulation results with reference values of simulation parameters

	FC	Electrolyzers
λ	0.01	0.01
$v_{H_2}\,[m/s]$	59.5	49.3
Re_{H_2}	1.19×10^6	9.87×10^5
$\dot{m}_{H_2,SinglePipe}\,[kg/s]$	6.64	4.87
$\dot{m}_{H_2,SinglePipe}\,[kg/h]$	2.4×10^4	1.75×10^4
n_{wells}	18	3
$V_{Storage}[m^3]$	1×10^9	

These parameters have been iteratively modified to evaluate their impact on the simulation and possible solutions to the related issues.

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4. Discussions of Results

4.1. Simplified Model

From the results of the simplified model we can clearly observe the impact of the chosen fuel cell - electrolyzers technologies on the required storage volume, even without considering the dynamic behaviour of unit operations. This choice directly affects, considering the range of efficiencies of the system, the amount of energy that has to be extracted (by electrolyzers) from the power surplus and the amount of energy that has to be actually stored in the form of hydrogen in the storage sites. This latter aspect is essential since it influences the dimensions of the underground artificial storage site in height and diameter, modifying the amount of freshwater (and, therefore, the environmental and economical impact) required for the construction process. These values can range, depending on roof depth, FC technology and cavern-freshwater volume ratio between $6.5 \times 10^6 - 7.2 \times 10^7 m^3$ for city 1, $1.6 \times 10^7 - 1.8 \times 10^8 m^3$ for city 2, and $9.7 \times 10^6 - 1.1 \times 10^8 m^3$ for city 3. These values are around 1% to 10% of annual Danish freshwater consumption.
Moreover, as it has been possible to highlight with the two scenarios, design choices in terms of storage placement and energy transmission can affect the cavern design and the system behaviour. System that can range from an offshore solution with main storage solution build under the seabed and electrical energy converted and transmitted from the hydrogen island to hydrogen production carried out in this dedicated artificial island, transmitted to land via pipelines and stored locally underground ready to be employed by the fuel cells system.

In the simplified model we ignored the inertia of the components of the system, e.g., fuel cells, electrolyzers, and compressors. Using the dynamic model, through running simulations for a 2 years time frame (with 1 hour resolution), we analysed the impact of the dynamic behaviour of each unit on the overall energy supply and demand. All these components have been implemented in a Simulink model, each one considering their fundamental working parameters and control systems. For the electrolyzers we included the start-up and ramp-up time intervals in the model and its blocks. Similarly it has been done for the fuel cells, applying the same parameters and blocks in the model. Concerning the compressor, based on its pressure-time dependency curve, a simplified control system has been implemented. Lastly, for the overall system, different control systems has been added. This Simulink model has been then exploited, as other functions that have been developed, inside a Matlab script with the aim of evaluating the storage volume, the number of electrolyzers and fuel cells wells and the mass flow rates through them respecting the pressure drop constraints and other model assumptions. This script has been iteratively modified changing the value of the main parameters of the system elements to visualize their impact on the overall system.

4.2. Dynamic Model

From the results of the dynamic model it is possible to analyse the sensitivity of the supply/demand system to the parameters that define the dynamic behaviour of its individual units. The first noticeable result is the storage volume difference between the static simplified model and the dynamic one: in the first case, the values obtained in the simulation are in the order of $10^6 m^3$, which can be covered by a few small to average-sized caverns (depending on the chosen FC-electrolyzers technologies considered and the characteristics of the cavern such as the roof depth). However, for the dynamic model we obtained required storage volumes in the order of $10^9 m^3$, e.g., around 1000 relatively large salt caverns. This 3 orders of magnitude difference between the two cases are related to physical constraints (mass flow rates of the pipelines and the following of the production and consumption curves), cavern pressure limits (i.e., $2.23 \times 10^6 - 7.09 \times 10^6 Pa$) and the start up times of the elements of the system (that do not allow the perfect following neither the production nor the consumption curves).
Moreover, choosing a fuel cell or electrolyzer technology with a high start-up time causes a system failure in following respectively the demand (in terms of shortage) and the production surplus curves (results not shown). This issue can be solved by developing or choosing components with lower start-up time or with predictive approaches to the system control, through which the components are activated earlier in time considering the predictions of production and demand. Components with high ramp-up times, instead, do not allow to fully exploit the potential of the power surplus (electrolyzers) or be able to supply the power needed by user in time: this problem may be solved with different approaches such as developing faster technologies, installing a higher number of these components to counterbalance the effect (but with additional investment costs and overdimensioning the system) or adding fast technologies (such as electrochemical storage) in parallel to mitigate this issue.
We also considered the fraction of surplus electricity to be converted into hydrogen and the initial storage filling percentage. The first aspect is important since considering higher fractions allows to increase the production of hydrogen thus being a possible mitigating solution for electrolyzers with high start-up and ramp-up time intervals. Higher fraction though results in higher number of components, higher mass flow rates and therefore an increase of the size of the system with consequent increase of complexity and costs. Moreover, it does not allow the electricity network to be integrated in a larger European network by exporting the surplus to other

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countries or regions with a high demand. Lastly, the initial storage filling percentage, also known as the cussion gas, is significant in the starting of the system since low initial level do not allow to have a sufficient buffer to follow the user demand; for this reason it is necessary to consider the initial filling as part of the installation procedure.

5. Conclusions

The large-scale storage of hydrogen in salt caverns, although a mature technology and relatively safe to implement, presents some important issues that have to be resolved. Firstly, the volume necessary to support even a simple 3-cities system is extremely high; it is challenging to find energy and water resources for the construction of around 1000 caverns and to find environmentally friendly and less energy-intensive solution to clean up and dispose off the construction and maintenance brine. Secondly, a large volume of cushion gas is required to start up the caverns such that it can reach a minimum required pressure for producing hydrogen from the caverns. This requires a large amount of surplus energy that might not be available. Thirdly, the high start up time of the fuel cells makes the use of hydrogen as the only grid balancing solution almost impossible. It is therefore necessary to address the immediate shortages of electricity in the network by other solutions, e.g., the aforementioned parallel electrochemical battery systems, or use reliable predictive models to deal with the not perfect following of the surplus and shortage curve by the components of the system. Finally, we would like to encourage the researchers in the field of subsurface hydrogen storage to dedicate more time and resources to investigating the production rate of hydrogen from the storage sites such as salt caverns, aquifers, and depleted reservoirs. The safe storage, although a necessary condition, is not sufficient to integrate the subsurface hydrogen storage in the energy supply and demand.

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