A thermodynamic and technical feasibility study of subsurface storage of energy in the North Sea abandoned reservoirs

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Abstract:

The oil and gas extraction from the Danish sector of the North Sea will soon end. Simultaneously, the existing and in development offshore windmills in the North Sea will ensure the availability of abundant and cheap electricity in the region yet fail to address the intermittent nature of the wind resources. This paper hypothesizes that the surplus electricity in the windy days and off-peak time can be converted to chemical forms (synthetic fuels, e.g., hydrogen, ammonia, methanol, or methane) and stored in the vast space of the abandoned oil and gas reservoirs under the North Sea. The stored energy can be extracted and consumed as carbon-neutral fuels or converted back to electricity when there is a shortage of wind. This work studies the technical and thermodynamic feasibility of offshore conversion of electricity to chemical energy sources and their storage/extraction in/from the North Sea oil and gas reservoirs. The technical feasibility study briefly deals with the sufficiency of the existing infrastructures including platforms and surface facilities to accommodate the process equipment for the conversion of electricity to chemical storable forms. Several processes including nitrogen and carbon dioxide separation from the atmosphere, electrolysis of seawater, and reduction of CO_2 and N_2 to synthetic fuels are simulated in a commercial process simulator. The thermodynamic analysis quantifies the exergy loss during the offshore conversion and storage/extraction of chemical energy in the reservoirs based on the results of an in-house open-source dynamic model that simulates the multi-component non-isothermal flow of fluids in the subsurface. The results show that the gas reservoirs with a higher permeability can store the large amount of energy that is required to address the wind energy fluctuation. However, depending on the future supply of wind electricity, a large energy loss in the process should be expected. Several technical problems regarding the electrolysis capacity, hydrogen turbines, and efficiency of compressors need to be addressed. Moreover, the estimated discharge rate from the subsurface storage can be too slow for addressing urgent surges of the electricity demand. Offshore subsurface storage seems to be a more suitable solution for the storage of chemicals to be used as transport fuel or raw materials that do not require high discharge rates.

Keywords:

Thermodynamic analysis, Electricity to fuel, energy storage, Energy transition

1. Introduction

The Ciara storm in February 2020, which was only partially felt in Denmark, increased the Danish wind electricity production to 1000 Mega Watts (MW) above consumption, that is equivalent to the average demand of one million European citizens. There were reports of significant curtailments up to several thousand MW from other countries in the North Sea region. Curtailment [29], which means accepting less renewable electricity than what windfarms can deliver is another word for wasted resources. these large amounts of wasted resources can be converted to nonvolatile chemical energy and stored in large subsurface reservoirs; how fast the energy can be converted and stored, how fast it can be reproduced, and how much of will be wasted in the process are the questions that will be answered in this work. The waste of energy from the windmills will soon become more severe when the North Sea is hit by a technological storm in the form of several large wind farms that are currently evaluated, planned, and licensed [1]. More importantly, since the electricity distribution is planned based on the unavailability of wind resources, the biomass (that is regularly switched to coal) power plants must always be running to compensate for the shortage of wind, thus emitting a large amount of carbon dioxide and other pollutants [34]. The solution is to store electricity when production is higher than demand and consume it when demand is higher than production [38].

The oil and gas extraction from the Danish sector of the North Sea has been declining, which will lead to the cessation of production and abandonment (i.e., plugging of the wells and removal of the facilities). Simultaneously, the existing and in development offshore windmills in the North Sea will ensure the availability of abundant and cheap electricity in the region yet fail to address the intermittent nature of the wind resources. This paper hypothesizes that the surplus electricity in the windy days and off-peak time can be converted to

chemical energy (synthetic fuels, i.e. hydrogen, ammonia, methanol, or methane) forms and stored in the vast space of the abandoned oil and gas reservoirs under the North Sea. The stored energy can be extracted and consumed as carbon-neutral fuels for transportation or be converted back to electricity when there is a shortage of wind. This paper studies the technical and thermodynamic feasibility of offshore conversion of electricity to chemical energy sources. The technical feasibility study deals with the sufficiency of the existing infrastructures including platforms, pipelines, and surface facilities to accommodate the process equipment for the conversion of electricity to chemical storable forms. Several processes including nitrogen and carbon dioxide separation from the atmosphere, electrolysis of seawater, and reduction of CO_2 and N_2 to synthetic fuels are simulated in Aspen Plus process simulator. The simulation results are used for the sizing of process equipment and the calculation of required platform area. The thermodynamic analysis quantifies the exergy loss during the conversion of electricity to fuel and back, and storage/extraction of chemical energy in the reservoirs based on the results of an in-house open-source dynamic model that simulates the multi-component non-isothermal flow of fluids in the subsurface [14].

There are three major questions that will be answered in this work. First, how much energy storage is needed in Denmark? This question is answered by quantifying the gap between the estimated future renewable electricity supply and demand. The answer helps to estimate the subsurface space required to address the intermittency issue of the wind electricity but does not discuss the expected dynamics of the storage process, i.e., the charge and discharge rate of the storage system. This leads to the second question that is answered here: to what extent can the subsurface storage be helpful in addressing the intermittency of the renewable electricity? Thirdly, what are the promising technologies from a technical point of view? This paper will provide simple, reproducible, and realistic procedures and quantitative answers to these questions. There are several major projects that have investigated the feasibility and associated risks of storing energy in the subsurface [9, 10] both onshore and offshore. Among these projects, the storage of hydrogen has gained considerable attention [26]. These investigations, however, are focused on the technical aspects of the subsurface fuel storage using the so-called thermo-hydro-mechanical-chemical (THMC) models, both experimentally and theoretically. There is no work that deals with the dynamics of the subsurface flow of fluids with the fluctuating supply and demand side of the energy network, which can lead to considerable loss of efficiency. The current work provide a preliminary answer to these concerns.

2. Future energy need of Denmark

The current plan for the developments of the wind farms in the North Sea is to quadruple the existing capacity of electricity production. Since the capacity is not equal to the actual produced electricity (due to, e.g. technical problems, curtailment, weather conditions, etc.) I will estimate the intermittent electricity production of the windmills by quadrupling the current electricity production in Denmark. The data is available from Energinet.dk website and also as a public repository [15], including several Matlab functions for data analysis and visualization. One can also assume that the domestic transport and heating will be fully electrified by 2050, which will add 50% to the current electricity demand [16]. It must be noted that these two assumptions, used here for the estimation of the future electricity supply and demand, are not written in stone and, in case of political agreements, can be of a temporary nature. The reader is therefore advised to use the outcome of the first section of the paper more cautiously. Even better, the reader can use the provided computer codes to update the assumptions with their own estimations that might be more realistic. The calculation procedure is based on the conservation of energy and thus fundamentally correct.

Fig. 1 shows the electricity supply and demand from May 2020 to January 2021 (left) and for the same period in 2050 (right). One can use Eq. (1) to integrate the data and obtain the average energy supply and demand over different periods of time, i.e. from 24 hours to nine month, as shown in Fig. 1:

$$\bar{E} = \frac{1}{t_2 - t_1} \int_{t_1}^{t_2} E\left(t\right) dt, \tag{1}$$

where $E(t)$ [MW] is the electricity supply or demand in the future and t_1 [s] and t_2 [s] represent a certain time period. The future energy supply and demand are estimated by using the correction factor extracted from [16], e.g.

$$E_{future} = \lambda_i E_{current}, \quad i = s,\, d \tag{2}$$

where $\lambda_d = 1.5$ denotes a 50% increase of the electricity demand [16] and $\lambda_s = 4.0$ denotes a 400% increase of wind electricity capacity in Denmark [4,13]. Note that this increase will be on the offshore sector only; however, here I assume that the overall wind energy capacity will increase by a factor of four. The other assumption in Eq. (2) is that the weather (more specifically, wind) in 2050 will be similar to the weather condition in 2020. The visualized energy supply and demand in Fig. 1 shows that periodically, the wind electricity supply is higher or lower than the electricity demand, creating periods with electricity surplus and shortage, respectively. The alternation between surplus and shortage can occur within a few hours to few weeks. This is better visualized in Fig. 2 that shows the average surplus and shortage for periods of 24 hours to 8 months. It can be observed that

after around six months, the average surplus and shortage reach a constant value. Repeating the calculations for different periods of 2019 and 2020 produced the same results. This plot unveils three critical pieces of information about the wind electricity supply and demand in 2050: first, the average shortage of electricity is 1.6 GW, which is a large amount of power and gives an indication of the amount of energy that needs to be stored (although sometimes the actual power shortage is temporarily higher as shown later). The good news is that the average electricity surplus is 2.25 GW, which is 620 MW higher than the average electricity shortage. These two numbers, however, serve as a constraint for the efficiency of the energy storage technology, i.e.

$$\eta_{storage} > \frac{\text{Average shortage}}{\text{Average surplus}} = 0.72.$$

This means that the efficiency of the storage technology must be higher than 72%. As was discussed in the previous section, this value is based on a number of assumptions and estimations that are uncertain. One can utilize the provided computer codes to recalculate this constraint with adjusted and perhaps more certain values for the future supply and demand of electricity.
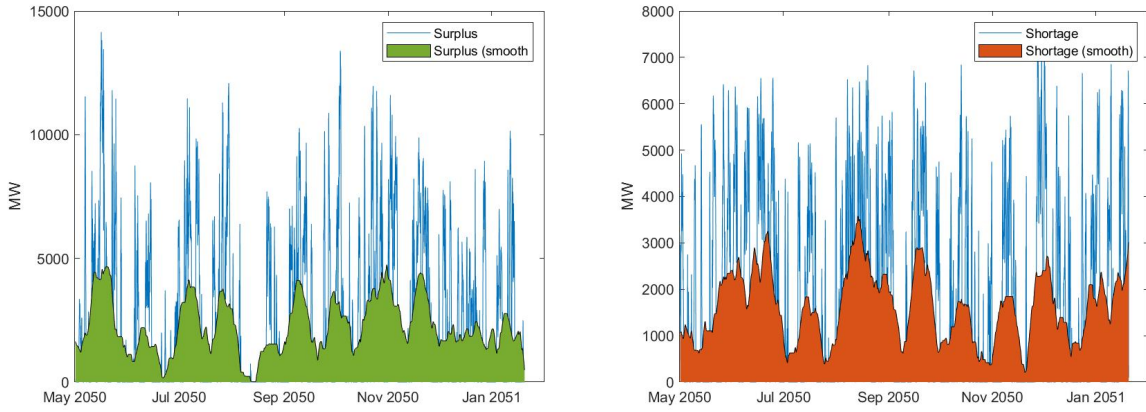

Figure 1: Electricity surplus (left) and shortage (right) adjusted for 2050; the smoothed curve is shown by area plot.
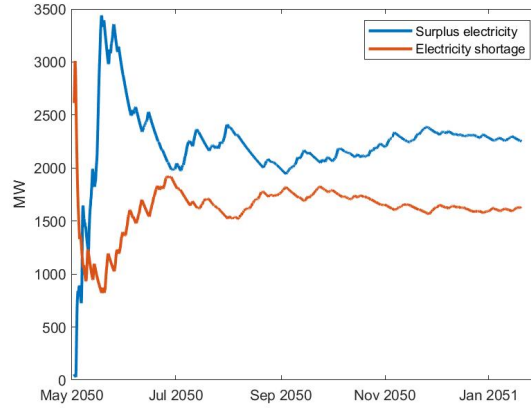

Figure 2: Average electricity supply and demand for Denmark adjusted for May 2050 to January 2051; the averaging is done using Eq. (1) by keeping the starting time fixed at May 2050 and averaging over gradually extending periods of time until reaching a non-fluctuating value.

Although the previous analysis provides the average storage value, the real time electricity surplus that needs to be stored varies with time. The same occurs with the electricity shortage, i.e. the occasional electricity shortage can be much higher than its long-term average value. Both of these values are shown in Fig. 1. Any feasible storage process must be able to store a maximum power surplus of 5.0 to 10.0 GW (see the peaks of the curves in Fig. 1-left) and recuperate the stored power with a maximum rate of 3.0 to 6.0 GW (see the peaks of the curves in Fig. 1-right). These values are critical in the design of the storage and recuperation processes. The sizing of the required equipment and sub-processes will be discussed in the next sections.

I end this section by estimating the subsurface volume that is required to store enough energy to cover for a eight month energy shortage. Table 1 shows the exergy per unit mole of different energy storage media that are studied in this paper. Exergy, ex_i [kJ/mol] is the amount of energy in a system that can be converted to

mechanical work, i.e. movement. The maximum efficiency of producing each medium, η_i, is also reported in Table 1. These values represent the highest efficiency of the state of the art technology for producing each chemical from the dead state in an electricity-driven process. For air, we assumed that the atmospheric air can be directly utilized without further treatments, thus the efficiency factor of 100%. For these calculations, one needs to have the density of the stored fluids at the reservoir conditions, T_{res} [K] and p_{res} [bar]. I used the typical reservoir conditions of the chalk fields in the Danish sector of the North Sea, i.e. 70°C and 200 bar. The volume of the reservoir is calculated by

$$V_{res,i} = \frac{\bar{E}_{shortage} t_{storage} MW_i}{ex_i \rho_i \varphi},$$

where $\bar{E}_{shortage}$ [kW] is the average electricity shortage, $t_{shortage}$ [s] is the period over which the electricity shortage is estimated (here 8 months), MW_i [kg/mol] is the molecular weight of the stored fluid, ρ_i [kg/m^3] is the density of the stored fluid at reservoir condition, and φ [-] is the porosity of the reservoir. Assuming a reservoir thickness of 100 m, the diameter of a chalk reservoir that can store the equivalent of eight-month electricity shortage in 2050 is calculated. The diameter is calculated assuming an efficiency factor of one for all the energy conversions. A 2 to 3 times larger reservoir volume is required if all the efficiency factors are included in the computations. All in all, the required volume for the energy storage is only a small fraction of the available reservoir volumes in the North Sea. Therefore, the reservoir volume is not a bottleneck in the subsurface energy storage. A reservoir with a thickness of 100 m and a radius between 100 m to 3000 m (considering the efficiency factors) can hold enough energy to compensate for 8 months of electricity shortage in Denmark in 2050.

Table 1: Exergy value and the efficiency of producing different energy storage media and the thermodynamic properties at reservoir condition (70°C, 200 bar); the efficiency factors are only considered for the electricity to fuel conversion.

Component	ρ [kg/m^3]	ex [kJ/mol]	V_{res} [10^6 m^3]	η [-]
NH$_3$	667.7	340	2.50	0.45
CH$_4$	386.6	831	1.66	0.36
H$_2$	67.7	236	4.21	0.7
CH$_3$OH	871.2	720	1.70	0.4
Air	733.5	22.0	59.89	1.0

3. Synthetic fuel storage

The conversion of electricity to carbon-neutral fuels, known as power2x, p2x, e-refinery, and several other names, is a topic that is extensively studied, e.g. [20, 22, 24, 28, 35]. To produce a carbon-neutral fuel, the raw material for the production of the synthetic fuels must come from the dead state, i.e. atmosphere and sea water. The dead state refers to the average composition of the atmosphere, Earth's crust, and oceans that theoretically does not have any potential to do work. Here, I consider the production of hydrogen, ammonia, methane, and methanol. The raw material for the production of these fuels are air and seawater and the only driving force for the production processes is the surplus electricity from the wind farms. From the atmosphere, nitrogen and carbon dioxide need to be separated. From the seawater, hydrogen will be extracted via an electrolysis process. These processes are discussed in the next section.

3.1. Nitrogen

Nitrogen can be extracted from the air through the cryogenic distillation of air. In this process, shown in Fig. 3, air is filtered, compressed, and liquefied by passing through a series of heat exchangers. The liquefied air then enters a high pressure followed by a low pressure distillation column. The separation of nitrogen from oxygen and other minor constituents of air is done based on the difference of their boiling points. Nitrogen is separated from the top side of the low pressure column. To liquefy air, a utility stream of around -200°C is required, that is often provided through the sudden expansion of a compressed refrigerant. Therefore, the entropy generation is high and the process is exergy-intensive. Different values are reported in the literature for the electricity consumption per unit mole of separated nitrogen. These values depend on the heat integration of the process. The largest value reported in the literature is around 15 kJ/mol air distilled. In our simulation, I obtained a value of 32 kJ/mol, which is perhaps due to the poor heat integration in the simplified simulations; thus, I used the value of 15 kJ/mol in our analysis.
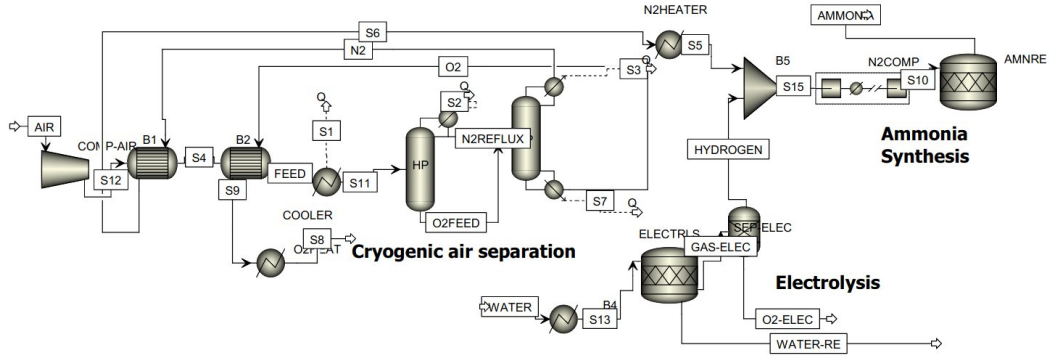
Figure 3: Ammonia synthesis process based on electrolysis and cryogenic air separation

3.2. Carbon dioxide

Carbon dioxide is a stable molecule that exist in a small concentration of around 40 ppm (40×10^{-6} mole fraction) in the atmosphere. Theoretically, it can be separated from the atmosphere by spending an energy amount that is equal to the chemical exergy of carbon dioxide [40], i.e.

$$ex_{CO_2} = -RT_{00} \ln x_{CO_2},$$

where R [8.314 J/(mol.K)] is the universal gas constant, T_{00} [K] is the dead state temperature (15^oC or 288.15 K in the North Sea region), and x_{CO_2} is the mole fraction of CO_2 in the atmosphere. This gives a value of 18744 J/mol, or roughly 20000 J/mol. Based on the previous experiences in the gas industry for the separation of low concentration acid gases such as CO_2, SO_2, and H_2S, the efficiency of such a process is quite low and rarely exceeds 5% [27, 32]. This means that the energy requirement for the separation of CO_2 from the atmosphere is around 400 kJ/mol or 9.0 MJ/kg CO_2. In practice, this number is around 10 MJ/kg CO_2 which is both accurate and memorable, although larger numbers are reported for the state of the art technology [5].

Besides being energy-intensive, the separation of atmospheric CO_2 (also known as air capture) has a large footprint since a large mass transfer area is needed between the air and adsorbents/absorbents; the footprint of the equipment is between 0.5 to 2 km^2 for capturing 1 million ton of CO_2 per year [3, 33]. This means that the direct air capture equipment cannot fit on a platform.

There are other ways of providing -close to- CO_2-neutral carbon sources, e.g. from biomass. The captured CO_2 from the industrial point sources, e.g. steel and cement industries or fossil fuel power plants, if the capturing and conversion to fuel is performed in a close cycle can also be carbon-neutral. However, these two sources are available onshore and it is therefore easier to utilize them as close to the source as possible. The other source of carbon is the remaining oil and gas in the reservoirs, which can be extracted by, e.g. insitu combustion. However, this carbon source is not sustainable and is not considered further in this study.

3.3. Hydrogen

Recent developments in the electrolysis technology has considerably increased the efficiency of hydrogen production from water. If the process is driven by the clean wind electricity, the produced hydrogen is a zero-emission fuel. Currently, hydrogen is included in all the energy scenarios for the countries in the North Sea region. For the offshore hydrogen production and storage, the following aspects need further investigations: fitting the water treatment, electrolysis, and compression equipment on a platform; pipeline integrity (for storage and gas transport); physico-bio-chemical interactions of hydrogen with the formation fluids and the chalk reservoir; capacity of reservoirs for storage of hydrogen and flow of hydrogen in the reservoir; energy efficiency and economic value of the process. Here, the energy requirement of the process, the size of the process equipment, and the flow of hydrogen in the chalk reservoirs will be addressed.

3.3.1. Green hydrogen production

Hydrogen can be produced from the electrolysis of water in the following reaction:

$$2H_2O \rightarrow 2H_2 + O_2.$$
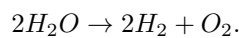
The minimum energy required for this reaction is given by the change of Gibbs free energy [39]. This reaction requires 39 kWh of electricity per kg hydrogen, but with the state of the art technology the value is closer to 48 kWh/kg [21, 37].

Hydrogen is purified by cooling it down to 308 K using cooling water. It removes the moisture from the hydrogen stream. The condensed water is recycled [39]. Some extra moisture remains in the hydrogen stream, which will be removed later in the intercoolers between the compression stages [39]. Electricity must be provided as direct

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current (DC), which introduces a loss of 2.5% for AC-DC conversion [39]. Rosen assumes an exergy efficiency of around 70% for the electrolysis of water for a mature electrolysis technology in 1995 (not considering other losses). He does not give more information on other steps of the process, e.g. water treatment and purification. There are several technologies to produce hydrogen from water using electricity among which two are more mature and are available as commercial packages, viz. alkaline electrolysis [12] and polymer electrolyte membrane cells (PEM) [8]. If the electricity is supplied by renewable resources, the produced hydrogen is called "green hydrogen" [23]. An efficiency of 60% to 70% is expected for these electrolysis processes, in which most of the energy loss is converted to heat. The energy loss during the compression of hydrogen will be calculated separately in the following sections.

The storage of hydrogen in the subsurface is a relatively old topic [37, 42]. Due to the high consumption of hydrogen, the petrochemical plants have been using salt caverns to store large volumes of hydrogen in the subsurface [37]. Currently, the subsurface storage of green hydrogen is being studied by several investigators in different continents.

There are several green hydrogen production projects being announced. Ørsted has announced that as part of the project H2RES, supported by The Energy Technology Development and Demonstration Programme (EUDP) under the Danish Energy Agency, a hydrogen production unit with a 2 MW capacity will be built by the end of 2021 [2] that will produce up to 1000 kg/day of green hydrogen. These capacities, although an step forward, will not address the GW scale energy shortage that will certainly occur due to the intermittent nature of renewable electricity, as was discussed in section 1..

The other issue that needs to be addressed here is the footprint of the electrolysis equipment. We saw in section 1. that the synthetic fuel production units are expected to consume several GW of surplus electricity. The main problem with these large amounts of power is that the electrolysis units are currently designed and built in MW scale. For example, one of the largest commercial PEM electrolysis units offered by NEL hydrogen has a capacity of 25 MW and requires 3×12 m^2 area for installation. Therefore, a 500 MW electrolysis plant that is made of 20 PEM cells is unlikely to to fit on a platform with other equipment although it is not impossible. A better option for the offshore hydrogen production is the installation of these electrolysis cells onboard a ship designed for this purpose. Otherwise, the onshore production of hydrogen seems to be the more realistic option.

Last but not least is the conversion of the stored hydrogen to electricity. Currently, there is no gas turbine that can work with pure hydrogen as a fuel. Therefore, the produced hydrogen must be mixed with a hydrocarbon fuel such as methane. This will cause some carbon dioxide emission unless a carbon capture process is used, which will in turn reduce the efficiency of the process. Fitting a GW scale turbine on a platform is possible but similar to electrolysis cells highly unlikely for GW capacities. As an example, Dan F host 6,800 tonnes of facilities and provides a power of 55 MW to the facilities. The highest point on the platform is 132 m above water. A typical 25 MW turbine that is designed for offshore platforms and consumes a mixture of methane and hydrogen weighs approximately 250 tonnes. Therefore, up to several hundred MW of gas turbine capacity can fit on a platform. But reaching to GW capacities can be a challenge.

3.4. Methane

Methanation process for the catalytic conversion of CO_2 and CO to methane was first suggested by Sendersen and Sabatier [11]. The reaction occurs in multiple steps starting with capturing of CO_2 or from an industrial or natural source or producing a mixture of CO_2 and CO by burning hydrocarbons (i.e. fossil fuels) or carbohydrates (i.e. biomass). In the presence of water vapor and at high temperatures, a considerable amount of CO and H_2 are also produced. H_2 can react with CO_2 and CO and convert them to methane. The reduction of CO_2 to methane by hydrogen is known as Sabatier reaction [11]:

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \qquad \Delta H_0 = -165 \,\text{kJ/mol.} \qquad (3)$$
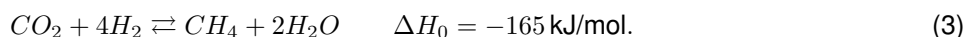
If the reactants, i.e. hydrogen and CO_2 are obtained from the dead state (i.e. seawater and atmosphere) using renewable electricity, the produced methane is carbon-neutral and sustainable. The reaction can be catalyzed by nickel or ruthenium and can be conducted in a packed bed reactor. The reaction rate in different ranges of pressure and temperature are reported in the literature. Although other reactions can occur at the high temperature and pressure of the methanations reactors, it is observed that the selectivity of the reaction towards methane is high [30]. A selectivity of close to 100% is observed for catalytic methanation of CO_2 over nickel catalyst at a temperature close to 300°C. Although theoretically the reaction reaches 100% yield at room temperature, in practice the reaction rate is too small and the methane yield is zero. A temperature of at least 200°C is needed to get the catalytic reaction started. At temperatures above 500°C, the reaction goes backward, i.e. conversion of methane and water to hydrogen and CO_2. This reaction is also known as methane reforming that is currently the main reaction for the production of the so-called "blue" hydrogen, i.e. hydrogen that is produced from a hydrocarbon. A schematic of the process for the production of green methane is shown in Fig. 4. In this process, the required hydrogen and carbon dioxide are produced by the electrolysis

of water and separation of atmospheric CO_2, respectively. The carbon source can also be provided from other alternative sources such as biomass or from the captured carbon dioxide from, e.g. cement or steel industries. However, capturing CO_2 from the atmosphere has the benefit of making the produced methane carbon-neutral or so-called "green". The reactor pressure is 20-70 bar [19] and the temperature is between 473 to 673 K. The overall efficiency of the produced methane is calculated by

$$\eta_{methane} = ex_{CH_4}^{ch} \left(\frac{4ex_{H_2}^{ch}}{\eta_{electrolysis}} + \frac{ex_{CO_2}^{ch}}{\eta_{capture}} + \frac{ex_{compression}}{\eta_{comp}\eta_{driver}\eta_{transmission}} \right)^{-1}, \tag{4}$$

where ex_i^{ch} [kJ/mol] denotes the chemical exergy of component i, and η_j [-] shows the exergetic efficiency [17] of the process j; $ex_{compression}$ [kJ/mol methane] denotes the exergy requirement for the compression of hydrogen and CO_2 to the pressure of the methanation reactor in a multistage compressor. Since the reaction is exothermic, I assume that the heat of reaction is sufficient to heat up the reactor to the required temperature of 673 K. By calculating the compression energy and replacing other efficiency factors from the previous sections, I obtain $\eta_{methane} = 36\%$. This is much lower than the expected value of 72%. Moreover, since this process requires a large footprint for the direct atmospheric capture of CO_2 and electrolysis of water, I do not consider it as a feasible option that can address the intermittency of the wind energy in Denmark. It is worth mentioning that this process can easily fit on a platform and if both hydrogen and CO_2 are provided, e.g. via pipelines, operating this process on a platform is viable.
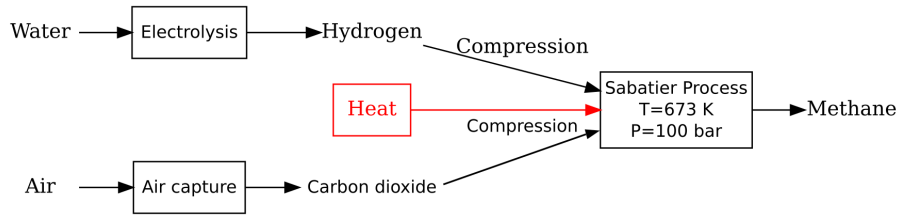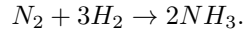

Figure 4: A block flow diagram of Sabatier process for the production of methane [16]

3.5. Ammonia

The block flow diagram of ammonia production is shown in Fig. 5. Ammonia is produced by an exothermic catalytic reaction between nitrogen and hydrogen:

$$N_2 + 3H_2 \rightarrow 2NH_3.$$

An ammonia reactor is operated at 200 bar and a temperature of 300 to 500^oC [18, 36]. The raw material for the production of ammonia, i.e. nitrogen and hydrogen, can be obtained from the air and seawater by the cryogenic air separation and electrolysis units, respectively. The nitrogen and hydrogen feed streams are compressed to 150 to 250 bar and react in a packed bed reactor at 673 to 773 K. The reaction is exothermic and therefore does not require external heating; it also produces high temperature heat that can be used in the process. The process can fit on a platform even for large scale ammonia production. However, as discussed before, the electrolysis unit for GW scale production of hydrogen does not fit on the platform. The cryogenic separation of nitrogen from air can fit on the platform; however, having long and heavy distillation columns (i.e. 60 theoretical trays) that work at very low temperatures on a platform can present several challenges for the stability of the platform and the extra room that is needed for the utilities. The efficiency of the process is calculated by

$$\eta_{ammonia} = ex_{NH_3}^{ch} \left(\frac{(1.5 + 0.21/0.79)\, ex_{H_2}^{ch}}{\eta_{electrolysis}} + \frac{ex_{compression}}{\eta_{comp}\eta_{driver}\eta_{transmission}} - ex_{turbine} \right)^{-1},$$

where the factor 0.21/0.79 indicates the number of moles of hydrogen that is consumed to burn oxygen for separating it from the nitrogen in the air. The efficiency of the new process for the production of ammonia is 43% which is lower but comparable to the 50% efficiency of the same process when nitrogen is separated in a cryogenic unit (see Fig. 3). It must be noted that currently there is no gas turbine that can operate on pure hydrogen and therefore the process can only be operational in the future.

Ammonia has the highest synthesis energy efficiency among the considered fuels because of the lower energy demand of nitrogen separation and the fact that hydrogen directly reacts with nitrogen with no need for sacrificing extra molecules of hydrogen to remove the oxygen atoms as is the case when carbon dioxide is used as a reactant [18].
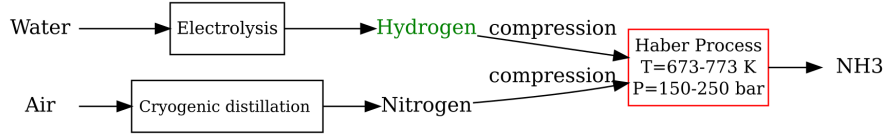
Figure 5: Haber process for the production of ammonia [16]

3.6. Methanol

Methanol can be synthesized from the catalytic reaction of hydrogen and carbon dioxide with the following reaction:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \tag{5}$$

The reactor operates at 100 bar and 264^oC [31]. The reaction is exothermic and therefore the system is cooled down by circulating water that produces steam. The material streams need to be compressed to 50 to 100 bar in the reactor. Compared to methane production in which two molecules of water is produced per molecule of methane, only one molecule of water is produced during the reduction of CO_2 to methanol. Therefore, even though the chemical exergy of methanol is lower than that of methane, the synthesis of methanol is slightly more efficient than the synthesis of methane. Similar to the methane and ammonia production, the efficiency of methanol synthesis is calculated by

$$\eta_{methanol} = ex_{CH_3OH}^{ch} \left(\frac{3ex_{H_2}^{ch}}{\eta_{electrolysis}} + \frac{ex_{CO_2}^{ch}}{\eta_{capture}} + \frac{ex_{compression}}{\eta_{comp}\eta_{driver}\eta_{transmission}} \right)^{-1},$$

which is estimated to be 40%.
The subsurface storage of methanol, however, is not advisable since methanol can be degraded by the subsurface microorganisms [41]. Therefore, I did not include methanol in our subsurface model, although only the input component name need to be changed in the attached Matlab script to estimate the energy efficiency of the subsurface storage of methanol (excluding the microbial degradation reactions).
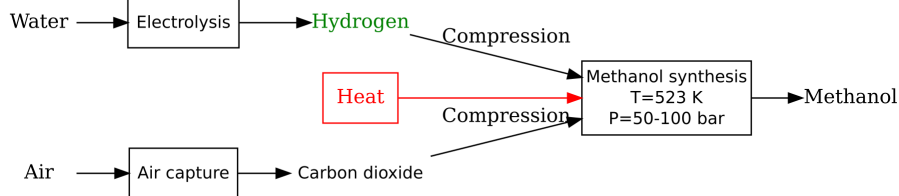

Figure 6: A schematic of the methanol synthesis process [16]

4. Subsurface energy storage

Although there are several reservoirs that can be used for the storage of energy, I can divide them into two main groups of sandstone reservoir (e.g. Harald West) and chalk reservoirs (e.g. Halfdan). Harald West is a sandstone gas reservoir at a depth of approximately 3500 m and a temperature of 135^oC. The porosity of the reservoir is 0.17 with a permeability of 1 to 50 mD in different layers. The thickness of the two high permeable layers (9 and 54 mD) is approximately 100 m. The Halfdan chalk reservoir is 2000 m deep with an average porosity of 0.31 and an average permeability of 3 mD. The wells in Harald West are vertical and the chalk fields are typically producing through long horizontal wells. In the case of a the vertical wells, I assume a thickness of 100 m for the reservoir, which means that a radius of 100 to 1000 m around the well will be utilized as the fuel storage space. For the longer horizontal wells, a smaller area around the well is required for the energy storage. I assume a well diameter of 5" for all the energy storage and production wells.

4.1. Problem formulation

I assume a gas reservoir represented as a cylindrical domain. The top and bottom of the reservoir are closed, i.e. no flow, and the outskirt of the domain can either be closed or at hydrostatic pressure. The top side of the reservoir is located at depth L [m], the thickness of the reservoir is H_{res} [m] and the radius of the well and the reservoir are $0.5D_{well}$ [m] and R_{res} [m] respectively. The injection rate is calculated based on the surplus electricity and the efficiency factor of the synthetic fuel production. The total injection velocity is calculated by

$$u_{inj} = \frac{E_{surpluss}\eta_j MW_j}{\pi D_{well} H_{res} ex_j^{ch} \rho_j},$$

where ρ_j [kg/m^3] is the density of the synthetic fuel j and is calculated at the bottom hole pressure and injection temperature (that is assumed to be close to the reservoir temperature). The bottom hole pressure is unknown

and is calculated by trial and error between the reservoir model and the injection boundary condition that is obtained from the above equation. The compression work for the injection of the gaseous fluid is calculated for the injection pressure of $p_{inj} = p_{bh} + \Delta p_{pipe}$, where p_{bh} [Pa] is the bottom hole pressure and Δp_{pipe} [Pa] is the pressure drop in the pipe that is calculated by the "pipe" unit in the software Aspen Plus.

I assume that for 2 months from 1st of October to 1st of December, we only store the fluids in the subsurface (when surplus electricity is available) and after that storage period, depending on the electricity supply and demand, we will have storage or production phases. The produced fluid from the reservoir is used for the supply of the electricity shortage; therefore, the discharge rate is determined by the electricity shortage. If the discharge rate is too high, the reservoir might not have enough driving force to produce the requested flow. In these situations, the bottom hole pressure becomes negative and the program produces an error. A better approach is to estimate the maximum productivity of the reservoir using an analytical solution [6, 7, 25]. This approach is not currently implemented.

4.2. Subsurface storage model

For the storage of the synthetic fuels in the gas reservoirs, I use a single-phase multi-component flow formulation. The storage of gas in the water flooded reservoirs is not a good idea since most of the gas will be trapped by capillary forces, and therefore will be permanently stored. It is possible to dry out the reservoir and prepare it for the gas injection by, e.g. injection of superheated steam or hot gases. However, it will require large amounts of energy and can potentially create thermally-induced fractures in the reservoir. I will therefore consider only the gas reservoirs for the storage of gaseous phase energy careers. For the liquid phase, I will use both gas and oil reservoirs. In both cases, I will include the compressibility of the fluids in the model as it is a major contributing driving force in the extraction of the fluids from the reservoir.

The single phase compressible flow in porous media reads

$$\frac{\partial}{\partial t}(\varphi \rho) + \nabla.(\rho \mathbf{u}) = 0, \tag{6}$$

where the Darcy velocity (assuming single phase flow and negligible gravity effect) is described by

$$\mathbf{u} = -\frac{k}{\mu}\nabla p, \tag{7}$$

The flow of the synthetic fuel in the subsurface is described by the advection-diffusion equation:

$$\frac{\partial}{\partial t}(\varphi c) + \nabla(\mathbf{u}c - \varphi \mathcal{D}\nabla c) = 0. \tag{8}$$

In the above equations, φ [-] denotes porosity, k [m^2] denotes permeability, ρ [kg/m^3] denotes the fluid density, p [Pa] denotes the reservoir pressure, μ [Pa.s] denotes the fluid viscosity, $\mathcal{D}$ [m^2/s] denotes the diffusivity of the synthetic fuel, and c [mol/m^3] is the concentration of the synthetic fuel. Both viscosity and density are functions of the fuel concentration. As discussed before, the injection rate in the well is a function of the supplied electricity that is obtained by the real surplus electricity data of 2020 adjusted for 2050. The above equations are solved numerically with the finite volume method. I performed the discretizition in the free Matlab software package FVTool [14] in a two-dimensional axisymmetric (i.e. cylindrical) coordinate. I used different permeability fields, including higher permeability near the wellbore region. A version with the possibility of adding fracture is also implemented.

5. Results and discussion

In this section, I discuss the results of the ammonia storage in the Harald West field. A radius of 20 m around the well is stimulated to obtain a permeability 100 times higher than the average permeability of the reservoir. This stimulation is necessary for the injection of the large flow rates that are required for the storage of energy in MW to GW scales. The withdrawal (or discharge) from the reservoir starts on 1st of December 2050 whenever there is an electricity shortage. The production rate is adjusted such that the bottom hole pressure is high enough, i.e. it can overcome the pressure drop in the well. I assume that 100 MW of the surplus electricity is provided to the ammonia production and storage unit in Harald West. As can be seen in Fig. 7, the injection pressure in the reservoir is only 150 bar higher than the hydrostatic pressure and thus within a reasonable range. The pressure fluctuation is between 200 to 350 bar, which can create geomechanical failure in the reservoir and needs to be further investigated. Once again, the production rate is controlled by the low permeability of the reservoir as can be seen in Fig. 8. To avoid a negative bottom hole pressure in the simulations, I imposed a discharge rate limit that is 20% of the maximum injection rate during the storage phase. With this limit, the efficiency of the electricity production (assuming an efficiency of 60% for the conversion of ammonia to electricity) from the stored ammonia is only 2.3%, which does not provide the 72% efficiency that is required for a feasible storage solution that can address the intermittency of renewable electricity production in the North Sea windfarms.
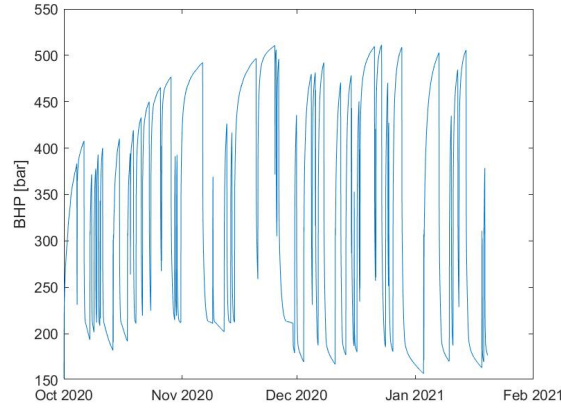
Figure 7: Bottom hole pressure (BHP) of the storage well in the Harald West ammonia storage facility
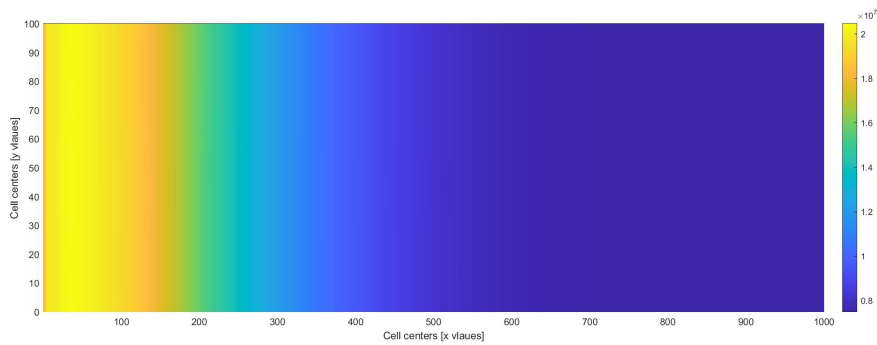

Figure 8: Pressure profile in the reservoir at the end of 4 months of ammonia injection and production

Finally, Fig. 9 shows the normalized concentration profile of ammonia in the reservoir after four months of injection and production. Ammonia has diffused to a 300 m radius around the well. Considering only the areas with a lower pressure as non-reproducible zones and by integrating the concentration of ammonia in those zones, an initial loss of 30% can be expected for the injected ammonia. One can expect that the synthetic fuel loss in the reservoir will not increase significantly and only occurs at the beginning of the storage process in which the reservoir is pressurized for the future re-production.
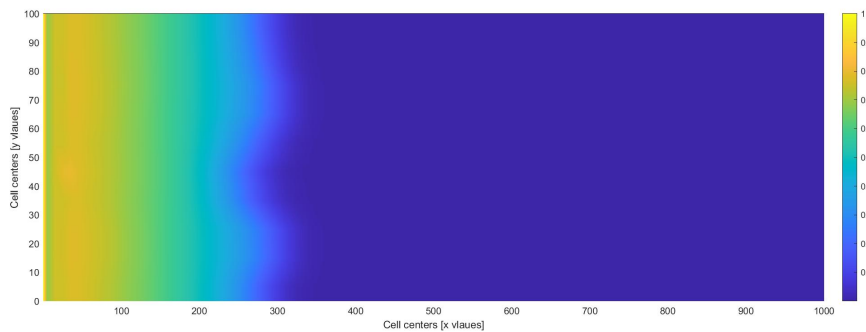

Figure 9: The concentration profile of ammonia after 4 months of storage and discharge in the Harald West reservoir

I repeated the simulations for the injection of synthetic fuels into a longer horizontal well; although the pressure profile is different and the pressure fluctuation is significantly reduced especially for the stimulated wells, the overall energy efficiency remains unchanged. This implies that the subsurface storage of physical and chemical energy must be performed in a confined zone, e.g. a salt cavern, instead of a large reservoir in which the fluids can spread due to the diffusive nature of flow in a porous medium.

6. Conclusions and suggestions

In this paper, I studied the possibility of the subsurface storage of the future surplus electricity that is produced in the North Sea wind farms in the form of synthetic fuels to address the intermittency of the renewable wind power. I showed that

1. Any potential energy storage solution must have an energy loss of less than 30%. Currently, only hydropower storage and batteries offer this efficiency, which are location dependent and only available in smaller scales, respectively. None of the studied synthetic fuels, with the possible exception of green hydrogen in certain conditions, can be produced with the required efficiency.

2. For 2050, a capacity of greater than 1000 MW electricity storage is required. The largest commercial hydrogen electrolysis units are in the order of 20 MW and have a relatively large footprint that makes them unsuitable for the offshore installations. Moreover, there is currently no hydrogen gas turbine in the market and hydrogen can only be utilized in hydrocarbon mixtures.

3. Methanol and methane require a large carbon source, e.g. CO_2. Air capture (the direct absorption of CO_2 from the atmosphere) is energy intensive and reduces the overall production efficiency of the carbon-based liquid and gaseous fuels. They also have a large footprint and do not fit on the offshore platforms. The only other option is the capture and transportation of CO_2 from the point sources by pipelines or ships to the platforms for the production of methane and methanol. The production processes can fit easily on a platform.

4. Ammonia is the most promising fuel by a relatively high synthesis efficiency and a low footprint (since it does not require a carbon source). I introduced a new design that does not need cryogenic air separation and is more suitable for the offshore ammonia production.

5. Recuperation of the stored fuel with the desired flow rate is a limiting factor in all the studied cases. It reduces the efficiency of energy storage to the unfeasible values of 1-2%.

6. A confined subsurface space, e.g. a salt cavern, is a more realistic alternative to the fuel storage in the North sea reservoirs.

7. Another potential use of the reservoir is for the permanent storage of carbon dioxide captured from the fossil fuel power plants and other CO_2 point sources, which can serve as a temporary solution during the green transition period. Moreover, the roll out of smart energy system and their integration with the subsurface energy storage can be investigated in the future.

Acknowledgment

References

[1] Global Offshore Renewable Map | 4C Offshore. Library Catalog: www.4coffshore.com.

[2] Orsted takes final investment decision on first renewable hydrogen project.

[3] Direct Air Capture: Resource Considerations and Costs for Carbon Removal, January 2021.

[4] Danish Energy Agency. About Energy Islands, March 2021.

[5] International Energy Agency. Direct Air Capture - Analysis.

[6] R. Al-Hussainy and H. J. Ramey Jr. Application of real gas flow theory to well testing and deliverability forecasting. *Journal of Petroleum Technology*, 18(05):637–642, 1966. Publisher: Society of Petroleum Engineers.

[7] Rafi Al-Hussainy, H. J. Ramey Jr, and P. B. Crawford. The flow of real gases through porous media. *journal of Petroleum Technology*, 18(05):624–636, 1966. Publisher: Society of Petroleum Engineers.

[8] Ugljesa Babic, Michel Suermann, Felix N. Büchi, Lorenz Gubler, and Thomas J. Schmidt. Critical Review - Identifying Critical Gaps for Polymer Electrolyte Water Electrolysis Development. *Journal of The Electrochemical Society*, 164(4):F387, February 2017. Publisher: IOP Publishing.

[9] Sebastian Bauer, Christof Beyer, Frank Dethlefsen, Peter Dietrich, Rainer Duttmann, Markus Ebert, Volker Feeser, Uwe Görke, Ralf Köber, Olaf Kolditz, Wolfgang Rabbel, Tom Schanz, Dirk Schäfer, Hilke Würdemann, and Andreas Dahmke. Impacts of the use of the geological subsurface for energy storage: an investigation concept. *Environmental Earth Sciences*, 70(8):3935–3943, December 2013.

[10] Sebastian Bauer, Tilmann Pfeiffer, Anke Boockmeyer, Andreas Dahmke, and Christof Beyer. Quantifying induced effects of subsurface renewable energy storage. *Energy Procedia*, 76(2015):633–641, 2015. Publisher: Elsevier.

[11] Andre Bolt, Ibrahim Dincer, and Martin Agelin-Chaab. A Critical Review of Synthetic Natural Gas Production Techniques and Technologies. *Journal of Natural Gas Science and Engineering*, page 103670, October 2020.

[12] Jörn Brauns and Thomas Turek. Alkaline Water Electrolysis Powered by Renewable Energy: A Review.

Processes, 8(2):248, February 2020. Number: 2 Publisher: Multidisciplinary Digital Publishing Institute.

[13] Matteo DAndrea, Mario Garzon Gonzalez, and Russell McKenna. Synergies in offshore energy: a roadmap for the Danish sector. *arXiv:2102.13581 [physics]*, February 2021. arXiv: 2102.13581.

[14] A. A. Eftekhari and K. Schüller. *FVTool: a finite volume toolbox for Matlab*. 2015.

[15] Ali A Eftekhari. simulkade/storage: The first release for the ECOS 2021 conference, March 2021.

[16] Ali Akbar Eftekhari. Quantifying the role of liquid hydrocarbons in the current and future energy balance of a self-sufficient Denmark. In *The 33rd International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems, Osaka, Japan*, Osaka, Japan, July 2020.

[17] Ali Akbar Eftekhari, Hedzer Van Der Kooi, and Hans Bruining. Exergy analysis of underground coal gasification with simultaneous storage of carbon dioxide. *Energy*, 45(1):729–745, 2012. Publisher: Elsevier.

[18] Said S. Elnashaie, Mohamed E. Abashar, and Abdulrahman S. Al-Ubaid. Simulation and optimization of an industrial ammonia reactor. *Industrial & Engineering Chemistry Research*, 27(11):2015–2022, November 1988. Publisher: American Chemical Society.

[19] Hanaâ Er-rbib and Chakib Bouallou. Modelling and simulation of methanation catalytic reactor for renewable electricity storage. *Chemical engineering transactions*, 2013.

[20] Matthias S. Frei, Cecilia Mondelli, Marion I. M. Short, and Javier Pérez-Ramírez. Methanol as a Hydrogen Carrier: Kinetic and Thermodynamic Drivers for its CO2-Based Synthesis and Reforming over Heterogeneous Catalysts. *ChemSusChem*, 13(23):6330–6337, December 2020. Publisher: John Wiley & Sons, Ltd.

[21] Dale Gardner. Hydrogen production from renewables. *Renewable Energy Focus*, 9(7):34–37, January 2009.

[22] Karim Ghaib and Fatima-Zahrae Ben-Fares. Power-to-Methane: A state-of-the-art review. *Renewable and Sustainable Energy Reviews*, 81:433–446, January 2018.

[23] Mikhail Granovskii, Ibrahim Dincer, and Marc A. Rosen. Exergetic life cycle assessment of hydrogen production from renewables. *Journal of Power Sources*, 167(2):461–471, May 2007.

[24] L. Guerra, S. Rossi, J. Rodrigues, J. Gomes, J. Puna, and M. T. Santos. Methane production by a combined Sabatier reaction/water electrolysis process. *Journal of Environmental Chemical Engineering*, 6(1):671–676, February 2018.

[25] Jacques Hagoort. *Fundamentals of gas reservoir engineering*. Elsevier, 1988.

[26] Aliakbar Hassanpouryouzband, Edris Joonaki, Katriona Edlmann, and R. Stuart Haszeldine. Offshore Geological Storage of Hydrogen: Is This Our Best Option to Achieve Net-Zero? *ACS Energy Letters*, pages 2181–2186, May 2021. Publisher: American Chemical Society.

[27] David W. Keith. Why capture CO2 from the atmosphere? *Science*, 325(5948):1654–1655, 2009. Publisher: American Association for the Advancement of Science.

[28] Joonas Koponen. Review of water electrolysis technologies and design of renewable hydrogen production systems. 2015. Accepted: 2015-04-23T10:08:56Z.

[29] Debra Lew, Lori Bird, Michael Milligan, Bethany Speer, Enrico Maria Carlini, Ana Estanqueiro, Damian Flynn, Emilio Gomez-Lazaro, Hannele Holttinen, and Nickie Menemenlis. Wind and solar curtailment: International experience and practices. In *12th International Workshop on Large-Scale Integration of Wind Power into Power Systems as well as on Transmission Networks for Offshore Wind Power Plants*, 2013.

[30] A. Loder, M. Siebenhofer, and S. Lux. The reaction kinetics of CO2 methanation on a bifunctional Ni/MgO catalyst. *Journal of Industrial and Engineering Chemistry*, 85:196–207, May 2020.

[31] William L. Luyben. Design and Control of a Methanol Reactor/Column Process. *Industrial & Engineering Chemistry Research*, 49(13):6150–6163, July 2010. Publisher: American Chemical Society.

[32] Maryam Mahmoudkhani and David W. Keith. Low-energy sodium hydroxide recovery for CO2 capture from atmospheric air - Thermodynamic analysis. *International Journal of Greenhouse Gas Control*, 3(4):376–384, 2009. Publisher: Elsevier.

[33] Noah McQueen, Peter Psarras, Helene Pilorge, Simona Liguori, Jiajun He, Mengyao Yuan, Caleb M. Woodall, Kourosh Kian, Lara Pierpoint, and Jacob Jurewicz. Cost Analysis of Direct Air Capture and Sequestration Coupled to Low-Carbon Thermal Energy in the United States. *Environmental science & technology*, 54(12):7542–7551, 2020. Publisher: ACS Publications.

[34] Peter Meibom, Klaus Baggesen Hilger, Henrik Madsen, and Dorthe Vinther. Energy Comes Together in Denmark: The Key to a Future Fossil-Free Danish Power System. *IEEE Power and Energy Magazine*,

11(5):46–55, September 2013. Conference Name: IEEE Power and Energy Magazine.

[35] Omar S. Mendoza-Hernandez, Asuka Shima, Hiroshige Matsumoto, Mitsuhiro Inoue, Takayuki Abe, Yoshio Matsuzaki, and Yoshitsugu Sone. Exergy valorization of a water electrolyzer and CO_2 hydrogenation tandem system for hydrogen and methane production. *Scientific Reports*, 9(1):6470, April 2019. Number: 1 Publisher: Nature Publishing Group.

[36] John C. Morud and Sigurd Skogestad. Analysis of instability in an industrial ammonia reactor. *AIChE Journal*, 44(4):888–895, 1998. _eprint: https://aiche.onlinelibrary.wiley.com/doi/pdf/10.1002/aic.690440414.

[37] Ahmet Ozarslan. Large-scale hydrogen energy storage in salt caverns. *International Journal of Hydrogen Energy*, 37(19):14265–14277, October 2012.

[38] Allan Schrøder Pedersen, Rune Christensen, Arghya Bhowmik, and Poul Norby. Energy storage technologies in a Danish and international perspective. 2019. Publisher: Technical University of Denmark.

[39] M. A. Rosen. Energy and exergy analyses of electrolytic hydrogen production. *International Journal of Hydrogen Energy*, 20(7):547–553, July 1995.

[40] Krishnan Sankaranarayanan, Jakob de Swaan Arons, and Hedzer J. Van der Kooi. *Efficiency and sustainability in the energy and chemical industries: scientific principles and case studies*. Crc Press, 2010.

[41] Diana Z. Sousa, Michael Visser, Antonie H. Van Gelder, Sjef Boeren, Mervin M. Pieterse, Martijn WH Pinkse, Peter DEM Verhaert, Carsten Vogt, Steffi Franke, and Steffen Kümmel. The deep-subsurface sulfate reducer Desulfotomaculum kuznetsovii employs two methanol-degrading pathways. *Nature communications*, 9(1):1–9, 2018. Publisher: Nature Publishing Group.

[42] Davood Zivar, Sunil Kumar, and Jalal Foroozesh. Underground hydrogen storage: A comprehensive review. *International Journal of Hydrogen Energy*, September 2020.