Power-to-X

Technology overview, possibilities and challenges

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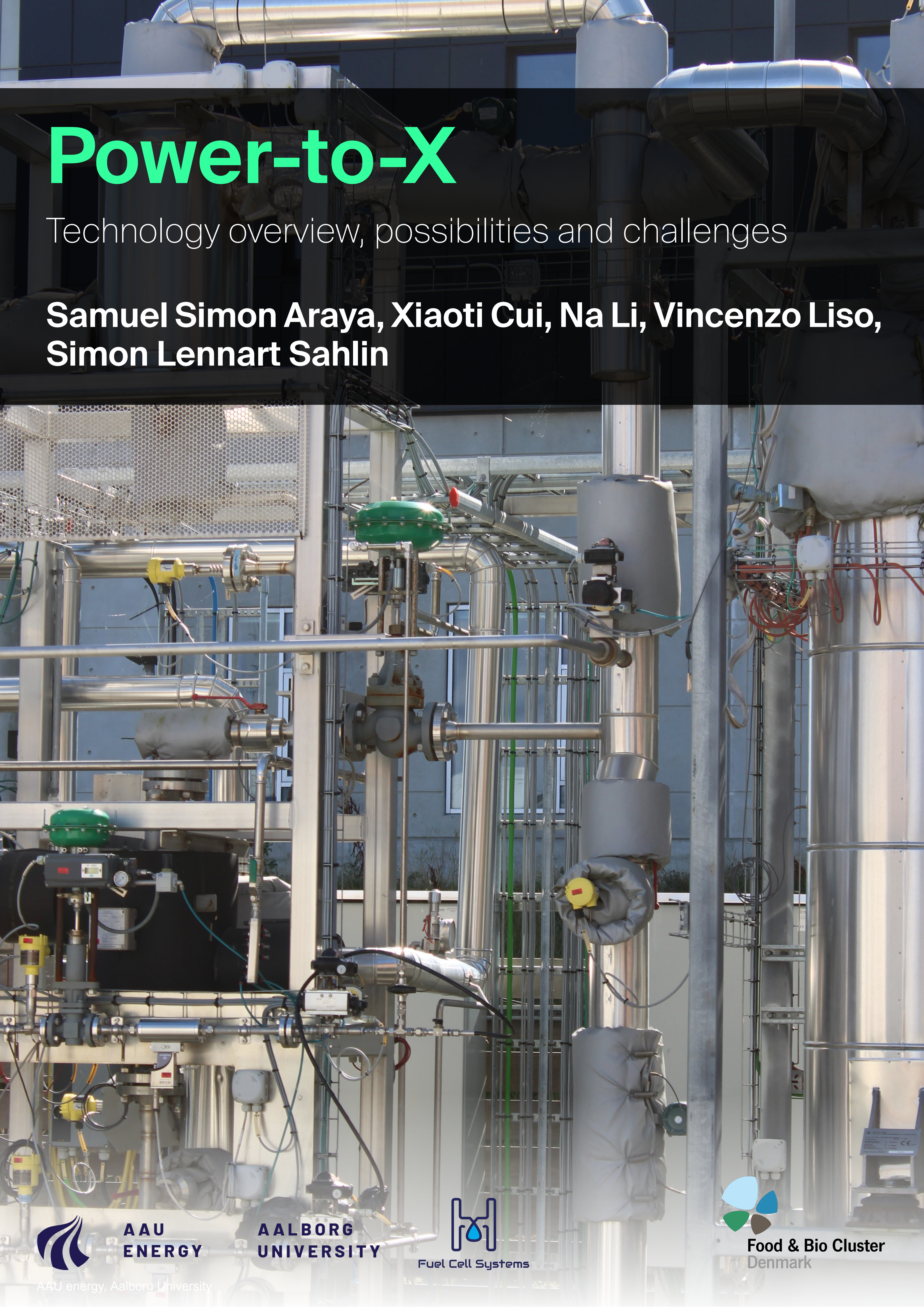

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Summary

This report gives an overview of the different power-to-X (PtX) technologies and their applications, including in production of efuels, heating, mobility, industry and proteins. It explores the opportunities offered by PtX and investigates the existing or potential future challenges that they can face, including the potential CO_2 bottleneck and ultra-pure water supply.

Deployment of more renewables and increasing electrification will contribute greatly in reducing our dependency on fossil fuels, but PtX is crucial to decarbonize the sectors of the economy that are hard to directly electrify. For this indirect electrification, the electricity source for PtX need to be excess renewable electricity from existing sources or from dedicated new and additional renewable energy sources, such as energy islands and offshore wind farms.

PtX technologies are expected to play an important role in the Danish strategy to achieve emission targets, and since several Danish companies are involved in the core PtX technologies, Denmark could soon become an exporter of PtX solutions, including export of green hydrogen. With the global market potential for hydrogen, methanol and ammonia increasing rapidly every year, there is a momentum of expanding market potential for PtX products. However, government incentives and policies to support the green transition are necessary in the early stages of the PtX era, as the cost of PtX products is still relatively high compared to fossil-based alternatives.

For PtX to succeed globally, it is crucial that new PtX plants do not compete with local resources, such as drinking water supply and use of agricultural land, and that they don't cause loss in biodiversity. Point source carbon capture (PSC) of CO_2 from industrial processes is attractive due to high concentration of CO_2 and the availability of numerous carbon-intensive and hard-to-abate industries. However, for long-term impact on the green transitions, sustainable CO_2 sources, such as from direct air capture (DAC) and from biomass-based processes should be favored.

Finally, the water demand in PtX is significantly lower than in many other industrial and agricultural processes. Nonetheless, since many areas around the globe that are suitable for renewable electricity generation are arid or semiarid, a careful planning is required to not disrupt the drinking water supply in those areas. On the contrary, it can be planned in a way that investment in PtX enhances the local water supply by boosting desalination and water treatment plants with better profitability from PtX products.

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Contents

Introduction

Increasing energy demand across all sectors of the economy and increasing urgency to transition from fossil fuels to avoid climate disaster call for alternative energy sources and solutions for decarbonization. In 2022, Europe is facing unprecedented energy crisis due its reliance on imported fossil fuels, with an import rate of the gross inland energy consumption totalling 58% in 2020 [1]. It is particularly worrisome and is the main cause of the current energy crisis that EU depends heavily on Russia for its fossil fuel imports, with 29% of extra-EU crude oil imports, 43% EU's natural gas imports and 54% of solid fossil fuel (mainly coal) coming from Russia in 2020 [1].

Deployment of more renewables and electrification wherever possible will play an important role in decarbonizing some sectors and reducing our dependency on fossil fuels. Though the cost of renewables is decreasing rapidly, with solar generation cost dropping by around 80% and wind generation by around 30-40% since 2010 [2], there are a number of sectors that will be difficult to directly electrify. Therefore, different solutions for decarbonizing all sectors are being developed to meet global and national emission reduction goals. One such solution is coupling renewable electricity to other sectors through hydrogen, where both renewable hydrogen and low-emission hydrogen are expected to have a major role in the clean energy transitions, especially in "hard-to-abate" industries [3].

A key way to decarbonize sectors of the economy that are hard to directly electrify is by using hydrogen produced from renewable energy sources and water via electrolysis. Renewable sources such as wind and solar are characterized by intermittency, i.e., they are produced according to the availability of wind or sun rather than according to demand. Therefore, an energy storage solution is necessary to overcome the supply and demand mismatch, which if done through hydrogen can either be converted back directly to electricity in fuel cells or can be further processed and used in other sectors than the energy sector. Synthetic fuels produced from hydrogen and other substances can be used in transportation, agriculture, industry and so on. This indirect electrification of different sectors is known as sector coupling, also know as Power-to-X (PtX).

This report gives an overview of the different PtX technologies and their applications, including fuels, heating, mobility, industry and proteins. It explores the opportunities offered by them and investigates the different existing or potential future challenges that PtX technologies can face, including the potential CO_2 bottleneck and ultra-pure water supply.

PtX technology overview

Power-to-X (abbreviated as PtX or P2X) broadly refers to converting renewable ”power” generation into an energy carrier (“X”) [2]. It describes processes that use surplus or dedicated renewable electrical power in other sectors via storage, conversion into other fuels, and successive re-conversion techniques. This is known as sector coupling, where the power sector is coupled to the transportation sector via power-to-mobility or power-to-fuel and power-to-gas; to the heating sector through power-to-heat, either via direct electrical heating or using heat pumps; and finally to the industrial sector, including the chemical sector through the use of the synthetic fuels and gases as a chemical feedstock. The concept of PtX is illustrated in Figure 1.

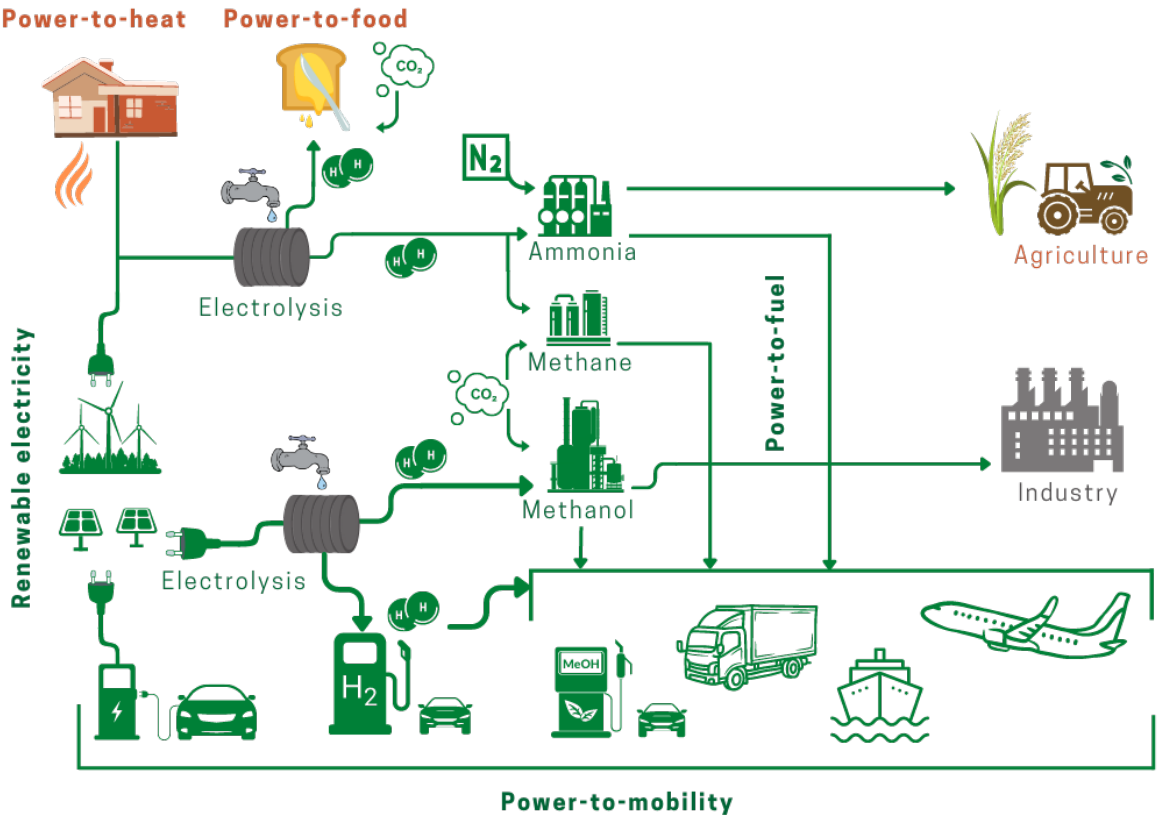

Figure 1: An illustration of PtX concepts.

The power in PtX could theoretically be generated from any source, however, if it is not of renewable origin, the whole purpose of transition from fossil fuels via PtX is defeated. Therefore, it is of paramount importance that the electrical power used in PtX is either surplus renewable electricity, where the PtX system also serves grid balancing purposes, or renewable power source dedicated to PtX (such as energy Islands), so that their demand does not worsen the electrical grid stability by adding more strain to the existing grid without any additional power sources. This way PtX can be used to help balance the demand and production of electricity, and thereby facilitate the renewable energy penetration and decarbonization of different sectors.

Other than water for electrolysis, PtX processes generally require other substances to produce synthetic fuels and chemicals. For instance, as can be seen from the illustration in Figure 1, the production of methanol and methane requires a CO_2 source and ammonia production requires N_2. CO_2 can be obtained from local renewable sources, such as CO_2 capture from the atmosphere or biomass sources, including biofuel and biogas plants, which at moment emit their CO_2 byproduct into the atmosphere [4, 5]. Moreover, there are hard-to-abate CO_2 intensive industries, such as cement factories that maybe interested in PtX solutions to reduce their carbon footprint, while also producing a valuable fuels and chemicals in the process.

Green hydrogen for PtX

Power can be directly used in several applications, including mobility, heating and cooling without first being converted into hydrogen. Nonetheless, hydrogen produced via the electrolysis of water using renewable energy is at the heart of the green transition via PtX. Electrolysis is a process that uses electricity to split water into hydrogen and oxygen. When combined with other substances, hydrogen can be transformed into different types of gaseous and liquid fuels, and other chemicals.

Generally, based on the production process and source of hydrogen, four different types of hydrogen can be named: black, grey, blue and green, in order of decreasing environmental impact [6]. Majority of the hydrogen produced nowadays comes from natural gas via a process called steam reforming, which however is fossil fuel-based and releases nearly as much CO_2 as when burning the natural gas. This type of hydrogen is called grey hydrogen, and when the CO_2 emitted during the process is captured and stored through a process called carbon capture and storage (CCS), then the hydrogen is known as blue hydrogen. Hydrogen can also be produced from coal via pyrolysis and the product hydrogen is called black hydrogen, which similarly to steam reforming causes CO_2 emission comparable to that of coal combustion. Finally, when hydrogen is produced via the electrolysis of water using renewable electricity, it is known as *green hydrogen* and doesn't have direct CO_2 emissions during its production. Green hydrogen is considered key in the effort to decarbonize the economy, as it can be used for sector coupling by storing renewable electricity in the form of gaseous or liquid fuels via PtX. Since all other sources of hydrogen cause significant CO_2 emissions, green hydrogen is the only viable hydrogen resource for the emerging PtX technologies. Hence, electrolysis of water is of paramount importance for PtX and progress in electrolysis technologies and reduction in the cost of renewable power is going to play a major role in the adoption of PtX technologies.

The commonly used electrolysis technologies are alkaline water electrolyzer (AWE), solid oxide water electrolyzer (SOEC) and proton exchange membrane water electrolyzer (PEMWE). These three main types of electrolyzers and their operating principles are illustrated in Figure 2.

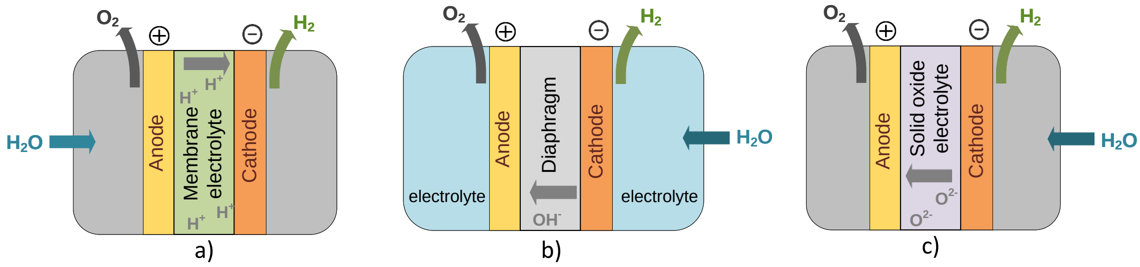

Figure 2: Schematic of the main types of electrolyzers a) PEM electrolyzer b) Alkaline electrolyzer c) Solid oxide electrolyzer.

Alkaline electrolysis

The alkaline electrolysis has a long history of development. Its working temperature is generally between 70 - 90°C, with alkaline solution as electrolyte (generally 25–40 wt% aqueous solutions of KOH or NaOH), which allows for the use of cheaper non-precious metal catalysts based on nickel, cobalt or stainless steels [7]. Water is fed to the cathode, hydroxyl ions are transported to the anode through electrolyte, and hydrogen is produced at the cathode side. AWE is the most mature technology among electrolysis technologies and is suitable for large-scale hydrogen production. The main disadvantages include higher operation cost caused by lower current densities as a result of higher ohmic losses due to the formation of bubbles, and safety issues due to high crossover of gases and stringent mass transport balancing requirements due to the risk of the intermixing of the bubbles [7].

PEM electrolysis

PEM electrolysis uses polymer electrolyte membrane as ionic conductor. The electrolyte, consisting of a thin, solid polysulfonated membranes, such as Nafion® and fumapem® [8], is used to transfers proton from the anode to the cathode side and separates hydrogen and oxygen gases. Advantages of PEM include, high proton conductivity, which translates to high current density, thin solid membrane that translates into compact system design and elevated pressure operation for easier storage. However, precious metal catalysts, such iridium and platinum, polymer films electrolytes and titanium-based porous transport layers used in PEMWE are expensive. Therefore, the balance of performance, durability and cost is the main factor that hinders the commercial penetration of PEMWE for hydrogen production.

Solid oxide electrolysis

Solid oxide electrolysis uses ceramic solid oxide electrolytes, such as nickel/yttria stabilized zirconia that conduct ${O_2}^-$ ions [8]. Water is fed to the cathode, oxygen ions are then transported to the anode through the electrolyte and hydrogen is produced at the cathode side. They operate at high temperatures between around 600 - 900°C, and since water is in steam and part of the energy required for splitting water is provided thermally, they can achieve higher efficiencies compared to other electrolyzer technologies. They also have the advantage of operating in reverse mode as fuel cells, which can be important for grid balancing services, since the same device can be use to produce hydrogen from excess electricity and then to give back electricity to the grid when the demand is high. However, their durability is limited due to the stringent material requirements that high operating temperatures entail. Consequently, long-term operation are yet to be shown, which slows their commercial deployment.

Other electrolysis technologies

More recent electrolysis technologies that combine some of the advantages of the other electrolyzer types include anion exchange membrane water electrolyzer (AEMWE) and proton conducting ceramic electrolyzer (PCCEL). AEMWE operate at temperatures between 40 - 60°C and uses polymer membrane similar to PEMWE, but in alkaline environment, which allows for the use of non-precious metals for the electrolysis process both on the anode and cathode side [7]. Therefore, it can be said that it combines the advantages of low internal resistance of PEMWE and cheaper non-precious metals catalysis of AWE.

PCCEL on the other hand operate in a similar manners as PEMWE with proton conducting ceramic, with similar electrode materials as SOEC. They have the advantages of higher efficiency due to higher operating temperatures compared to low temperature electrolysis, but the materials requirements for their operating conditions and their durability limit their development [7]. Both SOEC and PCCEL can operate in reversible mode, i.e., in electrolysis mode to store renewable electricity in hydrogen and then the process can be inverted and they can be used in fuel cell mode to produce electricity from hydrogen [9].

Lastly, there are microbial electrolyzers that use organic matter, such as biomass and wastewater to produce hydrogen [8, 10]. The electrolysis occurs when the active bacteria oxidize organic matter and generate CO_2, electrons and protons, and when external voltage is supplied the protons combine with electrons in the cathode to produce hydrogen [10]. However, the microbial electrolysis technology is still in early development stage and there are several challenges, such as low hydrogen production rate, high internal resistance, complicated design and material requirement that need to be overcome before they can be commercialized [8, 10].

Dynamic characteristics of electrolyzers

As the energy sources for electrolysis technology are mainly renewable energies such as wind and solar power, which are intermittent and fluctuating, quick dynamic response, lower dynamic range of operation, short cold start times etc. should be considered as a key factor during the operation. Especially, when the PtX system is intended for grid balancing, the choice of electrolysis technology should take into account the response time. It can be seen from Table 1 that PEM electrolyzer has the best dynamic characteristics among the three technologies and is the most suitable for intermittent operation.

Table 1: Dynamic characteristics for electrolyzers [11]

Dynamic characteristics	AWE	PEWE	SOEC
Cold start	$<$ 60 min	$<$ 20 min	$<$ 60 min
Lower dynamic range	10 - 40%	0-10%	$<$ 30%
System response	seconds	milliseconds	seconds

Other resources for PtX and their sustainability

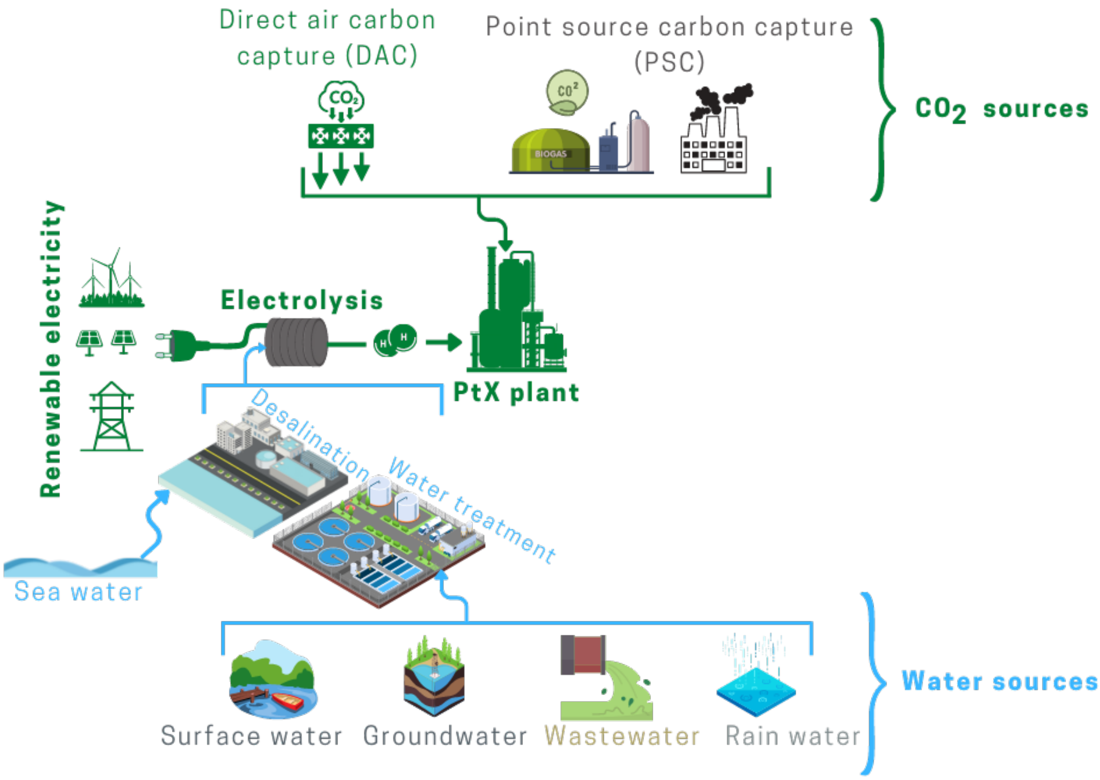

Figure 3: Sustainable water and CO_2 sources for PtX.

Since the whole idea of PtX is to decarbonize different sectors of the economy and help with the green transition to meet climate goals, it is only natural to consider the sustainability of the required resources. Therefore, it is of paramount importance that new PtX plants do not compete with local resources, such as drinking water supply and use of agricultural land, and that they don't cause loss of biodiversity, i.e., both water and CO_2 resources for PtX need to be sustainable [12, 13]. The different sustainable sources of water and CO_2 for PtX are illustrated in Figure 3. As already mentioned, the electricity source for PtX also need to be excess renewable electricity from existing sources or from dedicated new and additional renewable energy sources.

Sustainable CO_2 for PtX

Since all carbon-based e-fuels emit CO_2 during energy production, it is crucial that the carbon cycle is closed, meaning that a renewable CO_2 either from biomass or from the atmosphere should be used. CO_2 can be captured directly from the atmosphere in a process known as direct air capture (DAC) or from industrial process and biomass-based plants (biogas and biofuel plants), called point source capture (PSC), as shown in Figure 3. While CO_2 from DAC and biomass sources is sustainable and has closed carbon cycle, PSC from industrial processes doesn't have fully closed carbon cycle. Nonetheless, since our economy still relies on some industrial processes with hard-to-abate carbon emissions, using PSC from these industrial processes for PtX could offset some of these emissions. However, as more coal plants close and as the steel industry transitions to hydrogen, relying too much on industrial PSC can lead to the carbon bottleneck for PtX with increasing CO_2 demand. Therefore, sustainable CO_2 sources, such as DAC and PSC from biomass-based processes should be favored for a more farsighted approach. As can be expected, the cost of DAC technologies is still high for commercial applications at moment, but cost reduction is expected in the near future with further technological development and economy of scale.

Sustainable water sources for PtX

Generally speaking, the water demand of PtX is significantly lower than that of other industrial and agricultural processes. Electrolysis requires around 9-10 litres of ultra-pure water to produce 1 kg of hydrogen [14, 15], which is only a fraction of the water requirement of some agricultural applications, e.g., potatoes require 240 to 400 l/kg and rice requires 600 to 3400 l/kg [12]. Since, commercially available electrolyzers are sensitive to the impurities, ultra-pure water is required and depending on the water source and its salt and mineral content, the feed water could be up to three times the required ultra-pure water for electrolysis. The water purity requirement is normally defined by the electrical conductivity of water, which for alkaline electrolyzer cell is below 5 μS/cm and for PEM electrolyzers a stricter limit of < 0.2 μS/cm is required [16]. To achieve this water purity, different water sources need to be treated before they are fed to the electrolyzers for hydrogen production. Moreover, the amount of required water could more than double when considering system cooling as well, since electrolysis produces heat during operation. Nonetheless, even with the additional water needed for cooling and the water lost during purification, the water requirement for PtX processes globally is still relatively low compared to other applications.

However, large-scale PtX plants can cause significant disruption in water demand locally in some areas. This can be avoided by careful planning, where sustainable water source for the specific region is assessed and secured early in the plant design. Especially, for PtX to be a global success it is important to consider the scarcity of clean water in many areas of the world, including arid and semiarid areas that are usually considered suitable for renewable energy farms due to their weather conditions. Coincidentally, many of these places, especially the coastal areas have already plans for desalination plants to meet their increasing fresh water demands and PtX can act as a catalyst for these policies, as it can make the investments on desalination plants more profitable [12]. Concerns associated with desalination include energy intensity and potential negative ecological impact on biodiversity of the salt and chemicals in the brine [12]. Even though, desalination of seawater by reverse osmosis is the most energy intensive among water purification techniques, it is still less than 0.2% of the minimum energy required to produce the hydrogen by electrolysis, and cost of energy for desalination would only add $0.01 to the price of hydrogen per kg [15]. All other water sources, such as wastewater, groundwater and surface water are even cheaper and less energy intensive to purify compared to desalination. This leads to believe that water scarcity will not be the main problem in the adoption of PtX plans, as long as proper planning is done to avoid risk to local fresh water supplies.

The X in PtX: beyond e-fuels

The “X” in power to X can be several products that are used in different sectors; including gases (hydrogen, methane and ammonia); liquid fuels (methanol and its derivatives); heat (electrical heating and cooling, thermal storage in rocks); food (proteins), etc. The chemical products, especially, the gases and synthetic fuels can also be used as feedstock in the chemical industries.

Power to fuel

The main way PtX can help achieve the different climate goals is by substituting petroleum both in fuel applications and in the chemical industry. Especially, heavy transportation, including shipping and aviation, do not have an immediate green technology alternative on the horizon, and therefore, substituting the fuels will be crucial to meet climate goals. Fortunately, hydrogen, the most abundant element in the universe is the building block of all fuels, and even though, it doesn't not normally occur in its elemental state, its production from water and renewable electricity is getting more and more established. Below, the main fuels and chemicals that can be produced from PtX are described.

Power to methanol

Methanol has a great potential to substitute petroleum both as fuel for heavy-duty transportation or as green starting material for the chemical industry. It is the simplest alcohol, liquid at ambient conditions, with boiling and freezing points of 64.6°C and −97.6°C, respectively . Since it is easy to store and transport, it can serve as a convenient hydrogen carrier. As an e-fuel (fuel produced from electricity), it has a relatively high energy density. It has volumetric energy density of around 17.8 MJ/L [4], which is higher than that of liquid hydrogen and that of compressed hydrogen at 700 bar, and gravimetric energy density of 22.4 MJ/kg, which is around half that of gasoline [17].

Methanol produced from PtX is known as e-methanol, and its main ingredients are the renewable H_2 from water electrolysis and CO_2 from net zero emission sources. Compared to the traditional process the carbon source in the feed gas for e-methanol is changed from CO-rich synthesis gas to CO_2, which result in more water generation in the methanol synthesis reactor and will influence catalyst performance, reactor and process design. However, this modification work has been already achieved in demonstration projects, such as Power2Met project (Aalborg University, Denmark) and pre-commercial plant by CRI (Iceland) based on the mature technology from the traditional methanol industry. The technology for CO_2-based methanol synthesis process is currently considered to be close to large-scale commercialization stage.

Renewable CO_2 feedstock can come from biomass, such as biogas plants or from direct air captured (DAC) from the atmosphere. Alternatively, the so called '*blue*' methanol, uses CO_2 from Point Source Capture (PSC) from hard-to-abate and carbon intensive industries, such as cement factories [4]. Blue methanol still reduced the overall CO_2 emissions if used to replace petroleum in transportation or chemical industry.

Unlike a traditional methanol plant that runs continuously at certain operating load for a long time (e.g., half-year) with planned flow rate of feed gases, e-methanol plant is based on intermittent renewable electricity. The possible dynamic operations of the different parts of the plant (e.g., methanol synthesis and distillation processes, water treatment and water electrolysis systems) could be challenging if the plant is to respond to fast fluctuations of intermittent renewable sources. Therefore, optimal operation and control decision strategies and novel designs, considering the influence of dynamic operations on the entire power-to-methanol system should be investigated.

The e-methanol produced through PtX, which should meet purity specifications required on the market, i.e, "AA" or chemical-grade methanol or IMPCA methanol reference specifications, has several applications. It can be used as fuel in many application, both in internal combustion engines and fuel cells, it can be upgraded to jet fuel for aviation and its chemical derivatives and products can serve several sectors of our modern economy [4, 18]. A value chain of methanol with some of its derivatives and their application are given in Figure 4.

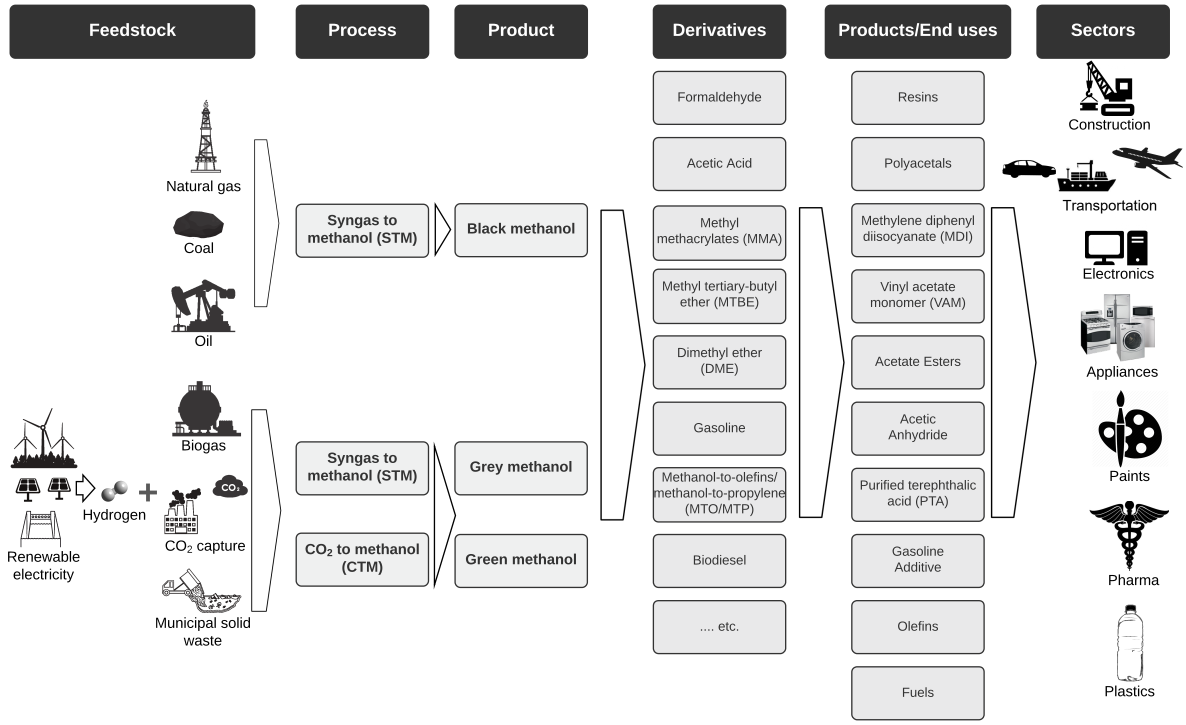

Figure 4: The methanol value chain. Modified from [4].

The more innovative and efficient way of extracting the energy from methanol is in Fuel cells, which are electrochemical devices that use the energy in the chemical bond of fuels to produce electricity. like batteries, they are composed of electrodes and electrolytes, but unlike batteries instead of storing electricity, they produce it continuously as long as they are fed with a fuel (methanol in this case).

The fuel cell variant that is best suited to use methanol as a fuel is known as high temperature proton exchange membrane fuel (HT-PEMFC) or alternatively reformed methanol fuel cell (RMFC). It operates at temperatures of around 160°C and uses phosphoric acid-doped polymer electrolyte called polybenzimidazole (PBI) as electrolyte, which allows to conduct protons in the absence of liquid water. To use methanol in RMFCs, it has to first be converted into a hydrogen-rich gas mixture via a process called methanol steam reforming in a catalytic reactor at temperatures of around 250-350°C. This is usually integrated in a system with the fuel cell, where some of the heat produced in the fuel cell is used to heat an evaporator that feeds the reformer and excess hydrogen-rich gas is returned back from the fuel cell to the reformer to provide heat for the reforming process via a burner unit. The overall system electrical efficiency in this case is around 40 - 45% and if the released heat is also used in combined heat and power application (CHP) the overall system efficiency can be significantly higher (> 90% [19]). The modularity of such a systems allows it to fit several applications, including in transportation and stationary applications.

Power to ammonia

Ammonia is colorless gas with a strong smell that can easily dissolve in liquid water and water vapor. Above 75% of global ammonia production is used as fertilizer, but it is also widely used as a refrigeration fluid and in household cleaning solutions [20]. The use of ammonia for power generation has recently drawn attention since many countries have initiated projects to use ammonia as carbon-free fuel for different applications. Ammonia, like other e-fuels can be used as hydrogen carrier to store and transport fluctuating renewable electricity. Ammonia has a better volumetric energy density than compressed gaseous hydrogen (700 bar) and liquid hydrogen, however conventional fuels such as petrol and diesel have substantially better volumetric energy density. It is relatively easy to compress and store liquid ammonia compared to hydrogen and natural gas, and it has a 50% more hydrogen compared to liquid hydrogen [21].

Compared to other e-fuels, which are mainly hydrocarbons, green ammonia has the advantage of being carbon-free, meaning that its production doesn't rely on expensive and not mature carbon-capture technologies or limited biomass resources. Moreover, its combustion or its use in fuel cells for energy production does not produce CO_2. This makes green ammonia more future proof, since it does not rely on CO_2 as a raw material, whose emissions we are actively trying to reduce. It is produced by reacting nitrogen and hydrogen ($N_2 + 3\,H_2 \rightarrow 2\,NH_3$), in a process known as Haber-Bosch process. The process involves two main steps: first hydrogen gas is produced, then it is reacted with nitrogen from air to produce ammonia. The two steps have been optimized, so that they can be integrated in a single plant.

The Haber-Bosch process, which is the main industrial method of producing ammonia currently, is an energy-intensive process, accounting for around 2% of the total energy consumed globally and 3% of global green house gas (GHG) emissions, making it the largest contributor to GHG emission from the chemical sector [22]. Furthermore, ammonia production occurs generally in large plants that produce thousands of tons of ammonia a day operating almost at steady-state conditions. It is estimated that ammonia is produced globally in just 550 plants, and only a few licensors can design and build these plants [23]. Considering that these plants have a long lifetime, ranging from 20-50 years, it will take several decades before the sector can become CO_2 neutral. China accounts for 30% of the global ammonia production with relatively younger plants compared to the rest of the world [23]. Therefore, though ammonia is already widely used in the industry, the entire ammonia synthesis sector will require several disruptive innovations to make the process CO_2 neutral and more suitable for integration with intermittent renewable energy sources rather than fossil fuels.

If green ammonia is used as hydrogen carrier for use in the energy sector, GHG emission reduction can be achieved by replacing fossil fuels in heavy-duty transportation, including maritime application. Researchers have been looking into other methods as well to produce green ammonia, such as the biological nitrogen fixation, where bacteria are used to synthesize ammonia. Moreover, the electrochemical production of ammonia directly from water and nitrogen using electricity is under investigation [24]. Both these methods have only been demonstrated in laboratory studies and the technology readiness level is generally considered low. Therefore, the most feasible method for large scale power-to-ammonia plants at the moment, is the mature Haber-Bosch process, which can be made sustainable by using hydrogen from water electrolysis and can be made more efficient by using absorbents in the reactor bed.

Power to heat (PtH)

Heating and cooling accounts for around 35% of the global energy consumption and around 51% of European energy consumption (only around 19% from renewable sources in Europe, 2018) [25]. While some heating and almost all cooling application are electric, further electrification of the sector is required to meet global green transition targets. Power-to-heating in this context refers to using renewable electricity in the heating sector, which can be achieved by powering heat pumps and electric boilers. Renewable electricity can also be stored in rocks and used for district heating [26]. In this combination, when used in conjunction with fluctuating renewable electricity, power-to-heat (PtH) can provide grid services by reducing the curtailment of renewable electricity, thereby increasing the stability of the electricity grid as the share of renewables increase. The concept of PtH is illustrated in Figure 5.

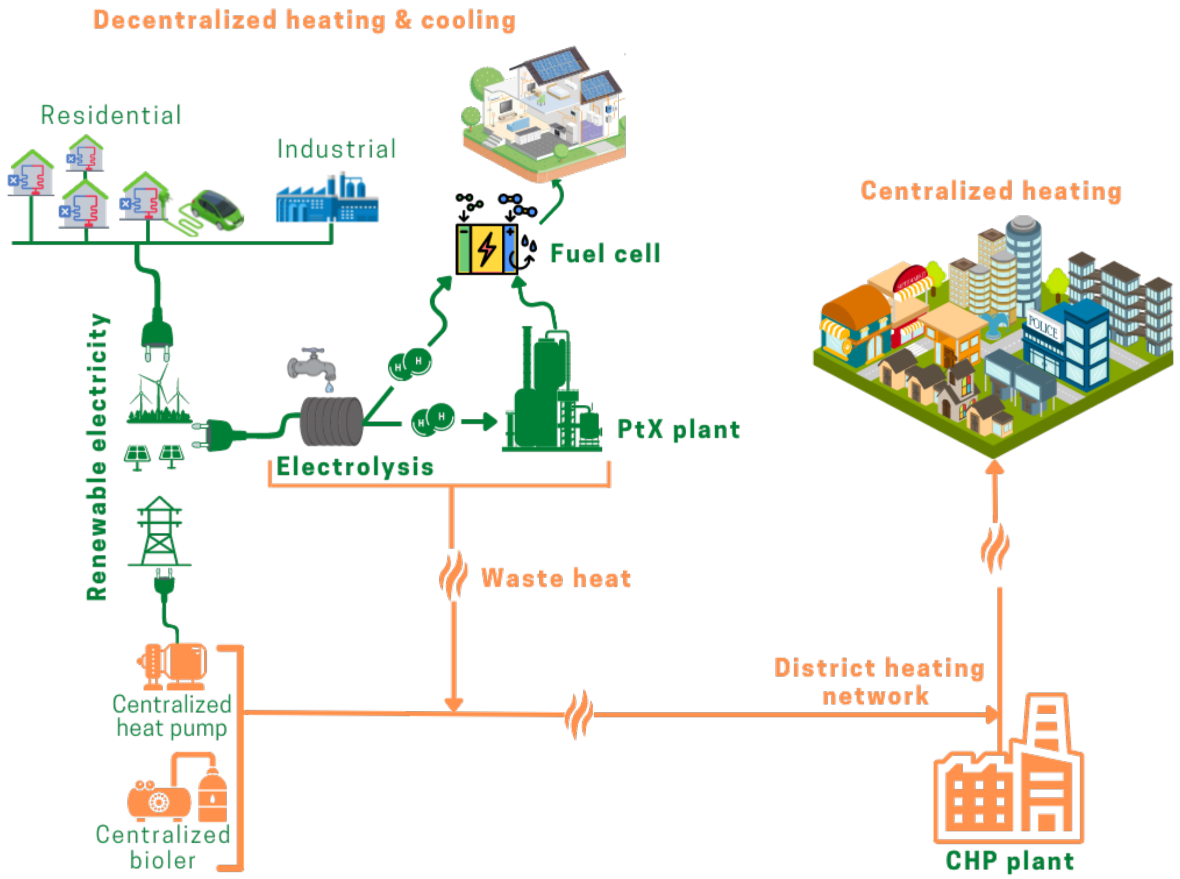

Figure 5: Power-to-heat concept.

PtH can be implemented in different ways and for different applications. It can be centralized and connected to district heating network with centralized heat pumps and electric boilers or decentralized for direct electric heating of residential buildings and industrial complexes. The fuels produced from the PtX processes can also be used for heating both in a centralized and decentralized setting, especially from power-to-gas plants. Methane can be injected into the gas grid both for heating and electricity production, the same way natural gas is used now. Both hydrogen and methane from PtX can be used in fuel cells to produce both heat and electricity in micro combined heat and power (μCHP) units for residential and industrial power and heating supply. As previously mentioned, methanol can also be used in HT-PEMFCs, which can be excellent μCHP units, owing to their high value excess heat.

Furthermore, excess heat produced from the PtX processes can be used in the district heating network. The different components of a PtX plant release different amount of heat during operation. It is estimated that from the electrolysis process and the auxiliaries of the PtX plant around 25% of the total energy supplied to the system is released as waste heat and can be integrateg to the district heating network as illustrated in Figure 5.

The role of agriculture and biomass in PtX and vice-versa

Biomass and agriculture to PtX

Biomass is already used for various applications as a sustainable alternative to fossil fuels. It is used for heating and electricity generation; for producing biogas and biofuels, both for transportation and the chemical industry, etc. At the moment, most of the excess CO_2 from this conversion of biomass to other products, the biomass-to-X (BtX) process, is emitted to the atmosphere [27]. Exhaust from BtX processes has one of the highest concentrations of CO_2 among CO_2 sources, e.g., 40 vol% from a biogas plant and 85 vol% from a bioethanol plant [28]. Therefore, they are ideal CO_2 sources for PtX plants. When integrating PtX and BtX, the process becomes power and biomass-to-X (PBtX), where carbon efficiencies higher than 90% can be achieved, vs. 25–40% of baseline BtX plants [27].

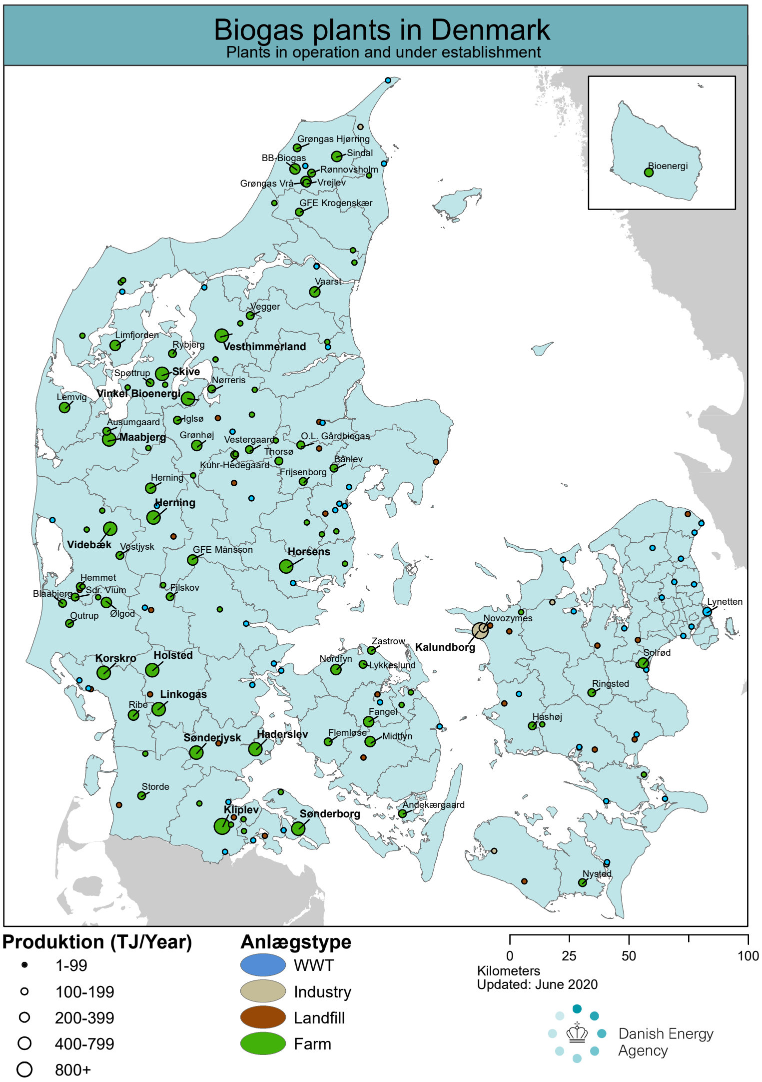

Figure 6: A map of biogas plants distribution in Denmark. Source: Danish Energy Agency [29].

Biogas production in Denmark is steadily increasing, with majority of the produced biogas used in electricity production and delivered to the natural gas grid after upgrading; and small amount used in other sectors, such as industry, transportation and heating [30]. The production was quadrupled between 2011 and 2019, with the part that is upgraded and injected into the gas grid increasing significantly in the same period [31]. According to the Danish transmission systems operator (TSO) Energinet, 25% of Danish gas consumption in 2021 was from biogas injected into the gas grid, which is expected to grow to 75% in 2030 and to fully phase out fossil natural gas in the national grid by 2034 [30]. These plans may be accelerated in the coming months or years due the energy crisis that Europe is facing as result of its reliance on imported natural gas, and power-to-gas could supplement biogas to facilitate the natural gas phaseout. Figure 6 [29] shows the map of biogas plants in operation and under establishment in Denmark.

During the biogas upgrading process, before injecting the biogas into the gas grid, high concentration CO_2 is released, which can be captured and used in PtX processes. With current annual biogas production of 15 PJ and expected more than 90 PJ by 2050 [29], there will be a significant increase in the renewable CO_2 source for PtX. With the development and further applications of CO_2 capture technologies, it is possible to capture CO_2 during the biogas upgrading process. Considering the potential 90 PJ biogas production in 2050, the CO_2 captured from biogas plants in Denmark could produce more than 2 million tons of e-methanol per year, requiring more than 2 GW electrolysis installations. However, PtX plants based on CO_2 from biogas plants are influenced by the scale and location of the biogas plants. Large centralized biogas plant in Denmark, e.g., with production of 800 TJ/year can provide CO_2 for the production of above 16,000 tons of e-methanol per year with around 24 MW electrolysis installation. However, this cannot be considered as a large capacity for methanol production compared to the traditional methanol plants that can produce up to 5000 tons/day.

The feasibility of CO_2 capture in biogas plants at different scales and possible CO_2 transportation strategy (e.g., pipeline construction) should be considered in the planning of PtX plants. Biogas contains around 30-45% of CO_2 and 55-70% of methane [32]. The CO_2 part in the biogas can be separated by possible CO_2 capture technologies, with different purity levels depending on the capture technologies. Then, the CO_2 can be stored and used in industrial application (e.g., food industry) or as a carbon source for e-fuel production for PtX process.

Besides e-fuels production from biogas, there are also possibilities to integrate PtX and thermal conversion of biomass. Typical biomass technologies such as hydrothermal liquefaction (HTL) and pyrolysis produce hydrocarbon gases, biocrude and char. Green hydrogen produced from electrolysis can be used for biocrude upgrading via hydrogenation, which can further reduce CO_2 emission from biomass processing compared to when using fossil fuel based hydrogen [33]. Hydrogen consumption for biocrude upgrading using HTL depends on the operating conditions, such as temperature and pressure; and oxygen and nitrogen contents of the biocrude, i.e., depending on the biomass source. Hydrogen consumption for HTL biocrude upgrading was reported at 6–14 mol H_2/kg biocrude [34], and for a biocrude production of 10,000 ton/year, the required size of water electrolysis is around 0.8–2 MW.

PtX to agriculture (Power-to-agriculture/food)

Due to the increasing need for green fertilizers to sustainably feed a growing global population and the transition towards the use of CO_2-free hydrogen-rich fuels, it is expected that the demand for green ammonia will dramatically increase in the future. Since ammonia synthesis currently accounts for around 3% of the global GHG emissions, there is great potential for emission reduction already by only electrifying the current ammonia production process for the current agricultural demands, i.e., by relying on hydrogen from water electrolysis rather than natural gas of fossil origins. A comparison between a natural gas-fed and an electrolysis-based Haber-Bosch process is given in [35], where the former emits 1.6 tons of CO_2 per ton of ammonia produced and the latter has no emissions. The majority of the CO_2 emission of the natural gas-fed system are due to the stochiometric CO_2 emissions, which are associated to the production of hydrogen during the reforming process. On the other hand, the electrically driven system has negligible emissions, which are mostly due to carbon footprint of the renewable energy input.

In addition to reducing GHG emissions from agriculture with green fertilizer from green ammonia, other PtX solutions can also be integrated in agricultural production processes. For instance, on-site green energy production and storage can avoid fuel transport and also promote low-carbon agriculture. A small-scale wind turbine, electrolyzer, compressor and storage tank located on a farm can provide electricity, heating, and hydrogen for fuel cell-based trucks and agricultural machinery. The produced oxygen can also be used for aquaculture, where fish and aquatic plants can be cultivated. From an economic point of view, the scenario is not yet cost-effective but is expected to be more competitive in the near future, as the cost of fuel cells and green hydrogen continue to fall. An illustration of how PtX in general can be used in agriculture is shown in Figure 7.

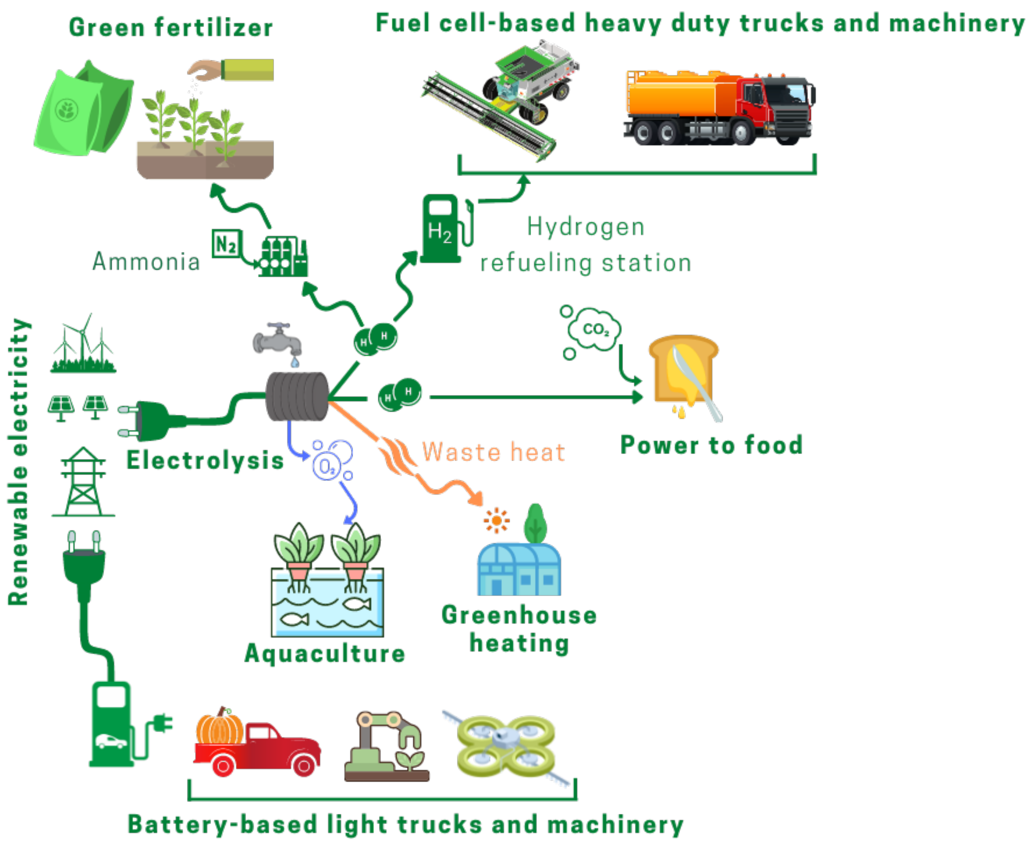

Figure 7: Agricultural concept based on power-to-X.

Hydrogen from electrolysis can also be combined with CO_2 to produce butters and oils in a process known as power-to-food or electrical photosynthesis [36]. However, power-to-food is is still in the early stages of development and more research effort and scale-up plans are required for it have a significant impact on the reduction of food sector's carbon footprint.

Current status and future prospects for PtX

Denmark is a global leader in wind technology, where on average around half of the country's electricity is generated by wind turbines. The government's goal is 70% emission reduction by 2030 and to reach climate neutrality by 2050 [37]. The country is on target to reach its emission target, already recording a 40% decrease in greenhouse gas emission in 2019 compared to 1990 levels and with plans in place across different sectors to achieve the remaining emission reduction gap until 2030 [38]. These ambitions will among other things push the development of green hydrogen and synthetic fuels in industry, light/heavy-duty road transport, shipping, aviation etc. The Danish government's target is to build large capacity electrolysis of 4-6 GW by 2030, which is expected to reduce 2.5-4 million tons of CO_2 emission [6].

Figure 8: The first e-methanol pilot plant in Denmark ($\sim$ 220 ton/year) at Aalborg University (Power2Met, EUDP project).

PtX technologies are expected to play an important role in the Danish strategy to achieve emission targets, and since several Danish companies are involved in the core PtX technologies, Denmark could become an exporter of PtX solutions, including export of green hydrogen. In fact, several companies and research institutions have conducted research activities on different aspects of PtX processes in recent years. Large research projects have been finished or are ongoing. For example, the first e-methanol pilot plant in Denmark was built in the Power2Met project at Aalborg University, AAU Energy premises in 2020 (shown in Fig. 8), with a capacity of 300,000 liters of e-methanol/year [39]. This was a successful project that catalyzed the conversation around PtX in Denmark and garnered the attention of companies like Maersk and circle K to use green e-methanol for shipping and road transportation, respectively [40, 41].

One of the largest PtX facilities in Europe is being built in the Høst PtX project in the city of Esbjerg in Denmark, which will be deploying large-scale industrial use of electrolysis technology on gigawatt scale to produce green ammonia from offshore wind energy [42, 43]. Integrating the waste heat from PtX plants with the district heating network and planning well for sustainable water sources will be important factor in the successful implementation PtX plants. In the Høst PtX project, treated wastewater will be used in the PtX plant [44] and the waste heat from the plant will be integrated with the district heating network and supply heat to around 15,000 households in Esbjerg, Varde and Fanø municipalities [43]. Excess heat from another PtX plant in Esbjerg will also be used in the Esbjerg city's district heating, where surplus heat from the production of hydrogen is expected to provide district heating equivalent to 200 households [45]. It is estimated that from the electrolysis process and the auxiliaries of the PtX plant around 25% of the total energy supplied to the system is released as waste heat, which based on a 2040 forecast for Denmark could corresponds to up to 10% of the current danish district heating production [46]. This can have a twofold effect of making both district heating and PtX plants cheaper by providing cheaper waste heat sources for district heating and adding value to PtX plants by monetizing their waste heat.

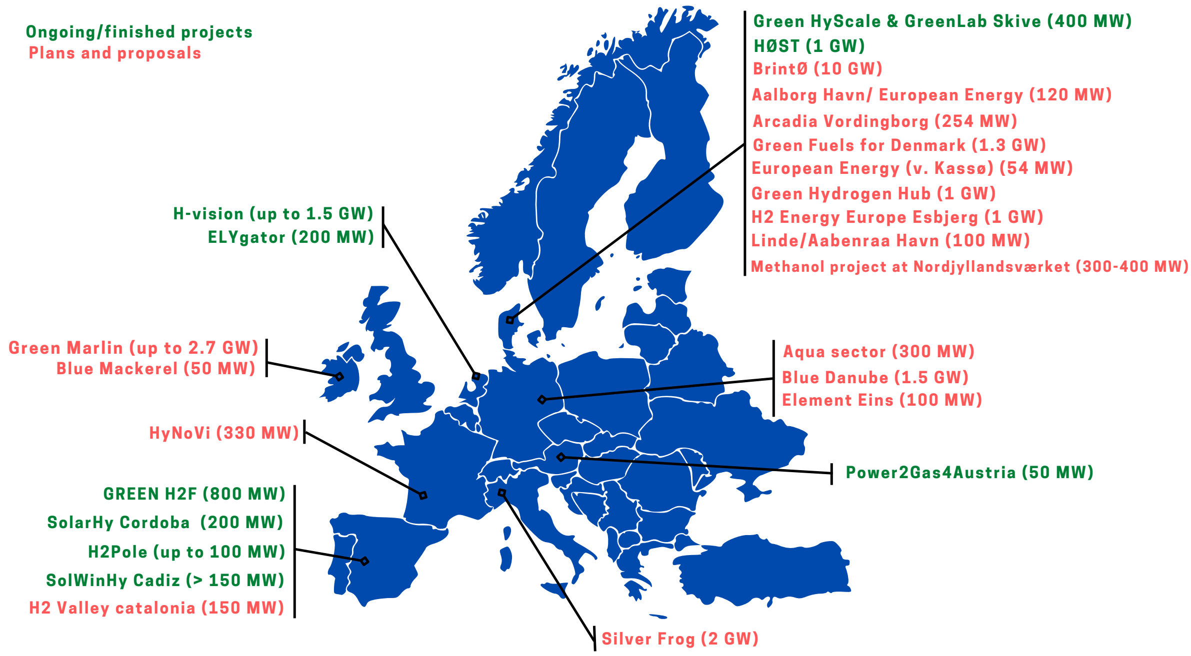

Figure 9: Notable hydrogen and PtX projects in Europe with capacity higher than 50 MW each. Sources: [47, 48]

At the time of writing this report, there are more than 40 PtX projects with more than 1200 full-time jobs and plans for the installation of 4 GW electrolysis capacity by 2026 in Denmark [48], significantly ahead of the 2030 targets. Whereas in Europe as a whole, there are more than 300 ongoing and planned hydrogen and PtX projects, more than 70 retrofitting/repurposing of existing infrastructure projects and more than 60 integrated hydrogen projects that encompass the whole hydrogen value chain [47]. In Figure 9, some notable hydrogen and

PtX projects in Europe with capacity higher than 50 MW each are shown, many of which are planned to reach their full capacity in 2030.

Globally, the market potential for PtX products is increasing rapidly. Methanol market is increasing at an average annual growth rate of around 7% to an estimated 91.53 billion $ global methanol market size by 2026 [4]. The global ammonia market, though it fell by 16.4% in 2020 due to the COVID pandemic, compared to the year-on-year growth between 2017-2019, it is projected to grow from $71.98 billion in 2021 to $110.93 billion in 2028 at a compound annual growth rate (CAGR) of 6.4% in the period between 2021-2028 [49]. Hydrogen market on the other hand is estimated to grow with a CAGR of 5% until 2030. Compared with the large market potential, the production of PtX products is still relatively small with very limited suppliers. Nonetheless, there is a momentum and expanding market potential for PtX products, which along with policy changes will be key to achieving the green transition and meet the global climate goals.

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