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Valorizing the Input and Output Waste Streams from Three PtX Case Studies in Denmark—Adopting a Symbiotic Approach

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Abstract: This study aimed to investigate the waste streams from the production of hydrogen energy carriers from PtX technology and identify how they can be valorized by applying a symbiotic approach to enable greater utilization of the inputs and outputs from such plants. Various electrolysis development projects are under development or in the pipeline in Europe and Denmark, but in many cases, it is not clear how waste streams are emphasized and valued in these projects. Thus, three exploratory case studies (a city, a rural, and an energy hub case) were investigated herein exemplifying state-of-the-art electrolysis projects currently being deployed, with a focus on identifying how and to what extent waste streams are being valorized in these projects and energy system integration is being pursued. Inspired by the industrial symbiosis literature, we analyzed how internal, regional, and long-distance symbiotic collaboration is realized within these cases and found them to be very different in terms of the energy carrier produced, the current development stage, and the access to appropriate energy infrastructure. This paper concludes that the co-location of PtX technology near biogas plants would provide a great opportunity for the integration of the produced energy carriers and waste streams into the existing energy system and, hence, could assist in stabilizing fluctuating renewable energy sources to enable their more efficient use in the energy system.

Keywords: biogas; circular economy; industrial symbiosis; power-to-X; waste streams

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1. Introduction

Renewable energy sources (RES) are a necessity in the ongoing transition of our current energy system away from the historic dependence on fossil fuels toward the use of more sustainable energy sources. However, the fluctuating and inherent unpredictable nature of RES makes it challenging to fully replace the traditional carbon-intensive energy supply based on fossil fuel. Hydrogen (H_2), as an important energy carrier with great potential, is regarded by many governments, researchers, the energy industry, etc., as a key player in the future [1]. Indeed, electricity and hydrogen are expected to be the dominant energy carriers in the future energy system, where it is expected that hydrogen will be stored and utilized for electricity, gas, and heat production, as well as producing various chemicals [2]. By storing the peak RES electricity produced from technologies such as solar PV and wind power as hydrogen, it is envisioned that the energy system relying on fluctuating RES could be stabilized and become more flexible to meet demand, allowing the current carbon-intensive economy to be decarbonized. This transformation is already underway today, and around 70 Mt of hydrogen is already produced on a global scale, with about 4% coming from electrolysis and the rest from steam methane reforming, as well as from the gasification of coal and oil [3]. However, it is still in the early days. Indeed, in the European region, electrolysis currently only accounts for about 2% of the energy mix [4]. Like many countries, Denmark is striving to decarbonize its energy supply and has committed to reducing its CO_2 emissions by 70% by 2030 compared to 1990 emissions and to become carbon neutral by 2050 [5]. As such, hydrogen and PtX production from RES—where PtX refers to "power-to-X" and is a collective term for electricity conversion technologies that can convert surplus electric power, such as excess load from RES, into carbon-neutral energy carriers (X) for use as synthetic fuels or chemicals, especially hydrogen—are regarded as offering a promising future pathway.

According to the Hydrogen Branch Organization (Brint Branchen) in Denmark, 43 hydrogen and PtX projects were announced in 2023, and if all the projects were to be realized to their full extent, this would correspond to 20–25 GW electrolysis capacity by 2030 [6]. This would far outstrip the target set out in the national Danish PtX strategy that was launched in December 2021, which set a political ambition of 4–6 GW electrolysis capacity by 2030 and is expected to reduce national emissions of CO_2 by 2.5–4 Mt annually. The strategy further stresses that PtX must be competitive with other technical applications, that it should benefit the energy system and infrastructure in Denmark, and that options for the export of PtX technology and deployment solutions should be emphasized [7]. The European Commission (EC) also has an ambitious PtX policy, in which they have set a target of 10 Mt annual hydrogen production by member states, as well as 10 Mt import of RES hydrogen by 2030, as stated in their REPowerEU initiative [8]. According to ref. [9], this would require 64 GW of installed electrolysis capacity within the European Union (EU), which must be implemented within only a few years to enable meeting the EU target. When adding the needed global capacity of 850 GW suggested by the International Energy Agency [10], the future PtX portfolio seems huge.

In the long term, the EU aims to be a zero-emission region by 2050—the world's first—and recognizes the need for clean hydrogen and PtX to achieve this. In A hydrogen strategy for a climate-neutral Europe, 2020 [11] and the Hydrogen roadmap Europe, 2019 [12], the European Union envisions a path consisting of three stages that will facilitate these goals: A first stage (2020–2024), in which the current PtX production is sought to be decarbonized, for example, in the chemical sector. This will require 1 Mt of RES hydrogen to be produced by 2024. In the second stage (2024–2030), 10 Mt of RES hydrogen should be deployed, and 40 GW electrolysis capacity installed by 2030 (equal to 8 Mt of hydrogen), and by then, hydrogen should be an integral part of the energy mix for new sectors, like, for example, rail transportation, the steel industry, and shipping. The ambition is that most of the electrolysis capacity will be generated near the user or the RES resources and should be a key part of an integrated energy system. In the third stage (2030–2050), RES hydrogen should be disseminated across all sectors, also embracing sectors that may be more difficult to decarbonize [8,9]. Ambiguous targets for hydrogen are hence envisioned for the future European market, and consequently, many PtX development projects are already in the pipeline in Denmark as elsewhere. In the following, we first exemplify several PtX development projects currently in the pipeline in Denmark and second describe some future energy island projects initiated by the Danish Government that are scheduled to be implemented before 2030.

1.1. Danish PtX Projects under Development and in the Pipeline

Ørsted and Skovgaard Energy: These two Danish energy companies are aiming to develop a PtX plant in Holstebro Municipality. The project—like most other PtX projects—will be built in several phases, with an aim that in the last phase, the plant will be expanded to an electrolysis capacity of 3 GW by 2030. Initially, the electrolysis capacity will be 150 MW. The RES utilized will be onshore wind and solar PV and later from offshore wind.

Ringkøbing-Skjern Municipality: The PtX project "Megaton" will have a planned electrolysis capacity of 2 GW when completed by 2030. The goal for the project is to produce 1 Mt of green fuel annually. In connection with the PtX plant, an energy park with a capacity of 4 GW of wind and solar energy is also being built. The project will cost around 60 billion Danish Kroner (DKK), equal to 8 billion euros.

Green Fuels for Denmark and Ørsted: The Green Fuels for Denmark project is led by Ørsted and connected to the company's combined heat and power plant (CHP), namely the Avedøre Power Plant. Many partners are involved in the project, including Haldor Topsøe, Nel, Everfuel, and Cowi as technology and knowledge partners, and A.P. Møller-Maersk, Copenhagen Airport, DFDS, DSV, and SAS as commercial partners due to their energy demand. The electrolysis capacity in the last phase will be 1.3 GW. By 2030, it is intended that up to 275,000 t of green fuel will be produced annually, considering an electrolysis capacity of 10 MW. Energy carriers like hydrogen and methanol will be produced, as well as kerosene, in the final phase, which should be sufficient to meet 30% of the annual demand for aviation fuel at Copenhagen airport.

Copenhagen Infrastructure Partners: Copenhagen Infrastructure Partners (CIP) is leading the "Høst" development project, which will be implemented in Esbjerg and is intended to produce green ammonia. The project has several partners and energy buyers, such as Esbjerg Municipality, DIN Forsyning, DLG, Arla, Danish Crown, DFDS, and A.P. Møller-Maersk. Høst should reach an electrolysis capacity of 1 GW and is expected to make Denmark self-sufficient in ammonia, with an annual production of about 600,000 t. The ammonia will be utilized in agriculture and shipping. The RES will be supplied by wind turbines and solar PV. The PtX plant will cover 30 ha and cost around DKK 10 billion (EUR 1.33 billion) and should be operational by 2027.

Three plants with 1 GW capacity each: Besides the four largest plants mentioned above, at least three other large projects are in the pipeline, all of which have an expected electrolysis capacity of 1 GW. These projects are H_2 Energy in Esbjerg, Green Hydrogen Hub in North Jutland, and HySynergy in Fredericia.

Considering all the projects mentioned above, around 10.3 GW of PtX capacity should be deployed before 2030, although this figure does not include some smaller plants also being implemented [13]. But, as mentioned earlier, up to 43 electrolysis projects were announced in Denmark in 2023, and if all were deployed, it would correspond to around 20–25 GW electrolysis capacity by 2030 [6].

Offshore energy islands and PtX: The Danish Government has decided to also support building up its offshore wind capacity. Development will take place on two artificial islands to be located in two spots in the North Sea and in the Baltic Sea near the island of Bornholm, respectively. The first energy island to be developed in the North Sea will generate 3 GW of wind energy by 2033 and 10 GW by 2040 and will also incorporate PtX technology to produce hydrogen directly on the island in the future. Ongoing discussions about whether to distribute electricity for electrolysis onshore or whether to produce this directly on the energy islands are still ongoing [14]. The final choice mainly revolves on the one hand, around the high costs of laying transmission cables from the energy islands to onshore facilities for electrolysis production and, on the other hand, on the benefits of using the power produced directly in electricity driven applications, instead of producing hydrogen alone, but with consequent energy losses [14,15].

1.2. Problem Field

As illustrated earlier, several Danish PtX development projects are currently in the pipeline, among which some are very large projects seemingly applying technical applications with no clear—or at least no transparent—vision of how to deploy the electrolysis production the most efficiently. This emphasizes the benefits for the energy system and infrastructure of generating capacity near the user—as prioritized by the EU—and the valorization of waste streams from the electrolysis process. The EU prioritizes integrated energy systems in their policies [16] and envisions PtX technology being adopted [9]. It is thus pertinent to ask whether the PtX projects currently in the Danish pipeline apply this approach. This also raises the question of how to integrate and deploy the technology to fit the contexts of the local communities, for example, regarding the supply of RES and water resources to the plant, and how to use the energy carriers (x) and waste heat to stabilize the fluctuating RES production. Such issues are important aspects to consider when adopting PtX technology and should be an integrated part of development projects.

Much of the literature on PtX has been published within the last decade, as shown in [3], and several emphasize the different energy carrier routes that electrolysis processes can provide. The research to date has mainly investigated the efficiency of systems, such as

PtMethanol, PtGas, and PtAmmonia, and pointed to the production of the energy carriers being feasible within the contexts analyzed [1,3,4,17]. This literature also emphasizes the different types of electrolysis technologies, such as AEC, SOEL, and PEMEL, and discusses the benefits and drawbacks of these technologies, e.g., [18,19]. However, there is scant literature seeking specifically to valorize the waste streams of PtX applications, and this topic is therefore underrepresented in the current academic literature, albeit a few studies specifically emphasize the potential for energy efficiency gains when using waste heat streams from PtX technology [20–23]. Most often, however, the *need* for waste stream valorization is just noted as a side remark when concluding the research findings [24,25], with comments about the need for utilizing and managing heat and oxygen outputs from the PtX process. Thus, there is a gap in the current literature focusing on the waste streams of PtX production and how they potentially could find usage in the future.

The contribution of this work is hence its emphasis on *which* types of waste streams exist and *how* to optimize the valorization of the waste streams connected to PtX production. This was approached by identifying symbiotic "markets" or "use potentials" for these outputs within or in proximity to the PtX plant in the community, region, or nationally. Options for stabilizing and utilizing the current energy system (electricity, district heating, and gas systems) were assessed with the consideration that they should provide synergies with already adopted technology/systems. This will be proposed from the point of departure of an exploratory case study approach by revealing the state-of-the-art deployment of PtX technology in Denmark, with a particular emphasis on waste stream valorization.

2. Materials and Methods

The following sections provide a description of the methodologies applied in this work, how data retrieval was achieved, and the theoretical approach utilized.

2.1. Data Retrieval

This section elaborates on the data retrieval aspects and the methodological considerations regarding data collection and outlines the study methodology and various parts.

2.1.1. Exploratory Case Study

We utilized an exploratory case study approach [26,27] for the cases investigated, as we did not have any pre-determined expectations of the outcome when entering the empirical research field. Also, when holding interviews as part of the data collection process, we approached the interview situations without exact knowledge of the stakeholders' positions on the topic investigated, the layout/design of the PtX applications adopted, and their emphasis—whether reluctance or welcoming—of valorizing the waste streams in connection with the electrolysis process. According to refs. [26,28], the use of exploratory case studies is also appropriate when researchers need to gain very detailed descriptions of a social phenomenon or when there is a need to explore and investigate presumed causal links that are too complex for a survey or experiment. According to ref. [27], case studies are appropriate when asking "how," "why," "what," and "who" questions. For the three exploratory case studies in the present study, qualitative semi-structured interviews were held with the three plant managers, one at each site, and information was also collected on a guided tour of each plant area to obtain more details on different aspects of each case. After the interviews, a summary of the information provided during the interview and at the site visit was immediately written, with any uncertainties or remaining queries resolved in follow-up telephone interviews [29]. The interviews followed the same format, guided by a "Questionnaire for Interviews", which can be found in Appendix A.

2.1.2. Case Study Design

Three case studies were chosen for this paper (see Section 3) in accordance with their different locations and plant layout/design. Case study 1 was the GreenLab Skive and PtX plant, representing a business and energy hub located near the city of Skive in the Northern part of Jutland. As the plant is situated in proximity to a range of industrial facilities, there are favorable opportunities to engage in symbiotic collaboration with the local community. The PtX plant is currently being constructed and will be developed further in the years to come. Case 2 is the Vinkel PtX plant, which is being developed as a stand-alone plant located in a rural area in the central part of Jutland. The plant is being implemented in the near future, and the main work will revolve around the biogas plant upgrading facility and current access to a natural gas network or gasnet. Being remotely located, the valorization of waste streams will be a particularly interesting topic to illuminate in the case study. Case 3 is a PtX plant that has just started operation and is being implemented in connection to a multi-utility company, DIN Forsyning, located in the 4th largest city in the Southern part of Denmark at Esbjerg harbor. As the PtX plant is located in the city, hence potentially near a heat market, this city center case study provides an interesting perspective on to what extent excess heat from the electrolysis process can be valorized. Moreover, it will also consider if other waste streams (input/output) than just excess heat can be valorized when a PtX plant is deployed in connection to a multi-utility company.

2.1.3. Literature Study

Besides the aforementioned case studies, a literature study was also conducted to qualify further information for this paper to use in the, e.g., introduction, problem field, methodology, and analysis. To perform the literature study, the relevant scientific literature was retrieved using search engines, such as Google Scholar, and inputting key phrases [30] such as “PtX technology efficiency”, “electrolysis pathways”, “hydrogen production and waste streams”, and “hydrogen energy carrier routes”. Generally, a literature study exemplifies the research within the field being studied and, as such, does not aim to provide a full review list of the published work within this research area, so we recognize that there are other relevant studies we have not cited herein. Moreover, reports from the European Commission, International Energy Agency, the Danish Government, etc., were utilized to outline the political agenda and the supporting policies for production from electrolysis within the European and Danish contexts.

2.2. Theoretical Outline

In the following section, we first elaborate on the symbiotic approach this work relied on to identify which waste streams exist in PtX plants and how they can be valorized, analogous to approaches taken in industrial symbiosis research. Second, a systemic investigation of the routes by which electrolysis is produced and eventually utilized was conducted to capture the important elements to be able to suggest how PtX technology could be deployed the most efficiently at its current stage. Several implications or focus areas to achieve valorization of the input and output waste streams were identified, which are presented ahead. Here, emphasis was placed on the resources, technology, hydrogen usage, processes, and integration of the energy carriers with the existing energy system in Denmark.

2.2.1. Symbiotic Approach

Symbiosis, which literally translates as an “interaction between organisms”, is a term frequently used in biology to describe the interdependence of species in eco-systems. However, the idea of symbiosis is also used in industrial systems, where, for instance, businesses trade waste and by-products to cut down on their resource usage. Symbiotic relationships between businesses thus refer to interdependencies formed via the exchange of by-products and/or shared infrastructure. The industrial symbiosis metaphor, which has its roots in the industrial ecology idea, first appeared in academic writing on industrial organization in the late 1980s [31]. According to refs. [32,33], the establishment of industrial symbiosis partnerships has the potential to close the materials loop, reduce energy usage, and hence create a more circular economic model for businesses. There are various types of industrial symbiosis systems, including (i) “classical” inter-firm collaborations between companies located near each other within a defined area, (ii) inter-firm collaboration between companies with symbiotic relationships that are located in the same region, and (iii) long-distance collaboration between companies [34]. According to refs. [34,35], at least three different companies must connect and cooperate by exchanging at least two different by-products before they can be recognized as being part of an industrial symbiosis.

The overall rationale of industrial symbiosis is for companies to simultaneously realize cost reduction and environmental benefits, essentially using the by-products and waste—or waste streams—generated by one company as the raw materials in another company. Furthermore, industrial symbiosis can also involve the sharing of infrastructure, such as buildings and facilities, energy and water supplies, and many other types of resources [36]. The difference between industrial symbiosis and industrial ecology is that the latter aims to build a sustainable closed system by combining industrial eco-systems, including aspects of industrial symbiosis, industrial metabolism, and consideration and response to environmental laws and regulations. Industrial symbiosis is, therefore, a means and a subset to achieve this, emphasizing exchanges to create synergy and thus reach the goals of an "industrial ecology" [37].

In this work, we used the concept of industrial symbiosis as a tool to analyze and assess the production and use of waste streams connected to PtX plants. Currently, PtX plants are being deployed in various ways and are connected to various industries or markets to enable a valorization of the inputs/outputs. This work, however, approaches industrial symbiosis from the perspective of considering the "markets" or "use potentials" for the waste streams from PtX plants and hence also looks beyond the sole focus on inter-firm collaboration to include other relevant arenas that potentially could enable a valorization of these waste streams. The use of waste streams within or in proximity to the PtX plant (i.e., classical inter-firm collaboration) could include, for example, residual water, CO_2, or oxygen (O_2); the use of waste streams within a region could include the use of waste heat for district heating purposes (i.e., regional collaboration); the use of waste streams within national boundaries (i.e., long-distance collaboration) could include, for example, the supply of electricity to the grid or pure methane to the gasnet. The systemic elements connected to electrolysis production in Denmark, especially in regard to the three case studies explored, are detailed in the following.

2.2.2. Systemic Elements Connected to PtX Plants

The context in which PtX plants can be deployed, or their planned deployment, will to a large extent define how the technology can be integrated and become a part of the local or national energy system and hence play an important role in the green transition to cleaner energy. Figure 1 provides an overall model of the usability (note: non-exhaustive) of the current PtX technology, with an emphasis on the AEC Alkaline Water Electrolyzer, which is currently the most developed and disseminated technology [19,38,39]. There are a number of critical elements to consider with PtX plants, as described ahead.

First, PtX plants need **Resources**, which generally consist of super-clean water and electricity. For the technology to become a part of the green transition, the electricity input should preferably be from RES, like wind power or solar PV. In this way, the PtX plants could assist in transforming fluctuating RES sources into more stable energy carriers. The cost of onshore RES is significantly lower than offshore RES and could, therefore, be prioritized in the initial stages of PtX development. Grid electricity could also be utilized, but this means the plant will not solely rely on green power unless the grid electricity is certified as green.

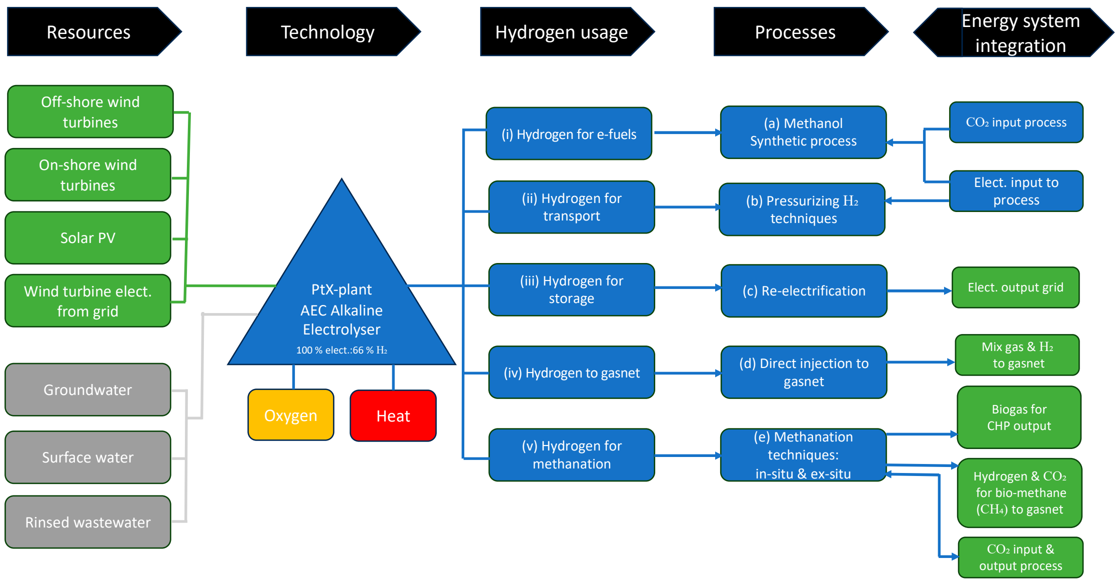

Figure 1. Systemic elements typically connected to a PtX plant.

The water demand in PtX plants is usually large, and the quality goes beyond just drinking water quality. Surface water or groundwater can be provided to the process, and additional cleaning of the water is then undertaken. On average, 150–200 kg of super clean water is needed per MWh of electricity used [40,41]. The wastewater from the rinsing steps to produce the super clean water could potentially be utilized as, e.g., secondary water in other processes. The water demand could, however, initially rely on wastewater, cleaned to the standard needed, to avoid taking drinking water from groundwater reservoirs in the electrolysis process [41].

Second, the **Technology**, namely the various technical elements of the PtX plant. Here, we focus on the AEC Electrolyzer, as emphasized earlier, which produces hydrogen with an average efficiency of 66%, besides waste heat and pure oxygen [38]. The amount of waste heat is significant and may comprise up to one-third of the total supply of energy to a plant [38]. This underpins the importance of locating PtX plants close to heat markets, such as large industrial facilities or local district heating networks, to facilitate a symbiotic use of this waste stream.

Third, the option for using hydrogen. There are generally five options for using hydrogen, i.e., the **Hydrogen usage**. These are illustrated in Figure 1 and can be described as follows: (i) the production of e-fuels for aviation and shipping, (ii) use of the hydrogen for transportation purposes, (iii) storage of the hydrogen for later usage, (iv) use of the hydrogen in combination with the natural gasnet, and (v) methanation of hydrogen, either to purify synthesis gas or to produce methane.

Fourth, the **Processes** are connected to the different usability routes, i.e., the various techniques and methods applied, which will, fifth, lead to different options for **Energy system integration**. These options include:

(a) Making e-fuel via a synthetic process, such as methanol, which would require an input of carbon (CO_2) and electricity from the energy system if not provided by local RES sources. The use of biogenetic CO_2 in this process could be supplied by upgrading the existing facilities (extraction of CO_2 from biogas to produce pure methane) connected to Danish biogas plants, or possibly from decentralized CHP plants fueled by biomass, such as residual straw or wood chips. The co-location of the PtX plant near such facilities would, hence, be beneficial. The use of biogenetic CO_2 is important from a symbiotic perspective, as in almost all cases, it would otherwise simply be emitted to the atmosphere from the biogas plants when upgrading their facilities. Currently, 675,000 t of biogenetic CO_2 are emitted annually from these energy plants [42], and thus not being valorized while also causing environmental issues, including contributing to global warming. Capturing and valorizing this output as a new input to the electrolysis process is therefore important, and carbon capture and utilization (CCU) could thus minimize this current wastage of biogenetic CO_2, which could be facilitated within the PtX plant via a classical "inter-firm collaboration".

(b) Pressurizing hydrogen to make it suitable as an energy carrier for transportation purposes, but this is an energy-intensive technique and will, in many cases, require an input of energy from the energy system to fuel high-pressure equipment unless energy is supplied from local RES sources. This process does not require carbon input.

(c) Storing hydrogen and eventually utilizing it for the generation of electricity, e.g., via re-electrification. In this way, it is possible to produce an output (electricity on demand) that could assist in stabilizing the fluctuating RES production.

(d) Injecting hydrogen directly into the gasnet [43]. Up to a 15% (potentially 20% in newer gas pipes) mixture of hydrogen and gas (methane) could be supplied and hence "stored" in an already established gasnet [44]. The stored energy within the gasnet could then later be utilized for, e.g., electricity and heat production or industrial usage, thereby helping stabilize the fluctuating energy supply from RES.

(e) Methanation, where hydrogen, for example, is converted to additional biogas via an in situ injection of electrolysis-produced hydrogen directly into the biogas' reactor tank [17]. This was investigated by ref. [45], which reported that up to 80% of the hydrogen was converted to methane, and between 40–60% of the biogas' content of CO_2 was removed. Alternatively, new ex situ co-located technology—like a biological methanation facility—could be established separately, where biogenetic CO_2 from an upgrading facility could be utilized and combined with hydrogen from the PtX plant in the following process [17,22]. According to ref. [46], such a separate (ex situ) methanation plant could typically increase the biogas yield by up to 42%.

A mechanization plant could also be deployed without the upgrading facility, in which raw biogas, which consists of roughly 40% CO_2 and 60% methane [47], could react with hydrogen from the electrolysis process. The biogas could then be used for combined heat and power (CHP) production to provide district heating to citizens and power to the grid. An option here could be implementing the upgrading facility after the biological mechanization process to increase the gas yield (i.e., biomethane) even further. The key input for the latter example is—besides hydrogen from the electrolysis—biogenetic CO_2 from the biogas plant upgrading facility, as well as CO_2 from the raw biogas from within the methanation plant. The methanation processes described earlier provide for a more circular and symbiotic usage of waste streams and can result in the provision and promotion of energy system services, like providing biomethane to the gasnet or/and biogas to drive motors/generators for CHP production, hence displaying an integration with the existing energy system and stabilization of the fluctuating RES sources. As far as technology maturity, there is, however, still a critical need for research and optimization of the ex situ methanation technology, while in situ technology has so far been proven to be more reliable.

2.2.3. Valorizing Waste Streams and Energy System Integration

As seen from the systemic elements detailed in Figure 1, 'Hydrogen usage' via the '*Process*' of 'methanation' can potentially facilitate high energy system integration, whereby many synergies and energy services could potentially be obtained. This would also provide favorable options for stabilizing the fluctuating energy system from RES, as well as for storing and converting the hydrogen by utilizing already existing technical applications and energy infrastructure. This could be, e.g., gas and district heating networks, the use of CO_2 via CCU from the already established biogas plants, or the methanation of hydrogen via various techniques applicable at already implemented Danish biogas plants. Hence, the need for immediately investing in new highly expensive infrastructure in connection with PtX [48] could be avoided, and the maturation and dissemination of PtX technology could be coupled to existing and new biogas technology and could occur as a parallel process. Hydrogen pipes and extensive expansion of the electricity grid could, therefore, be implemented at a pace that follows the actual development and upscaling of the current electrolysis technology.

In the exploratory case study discussion, presented in Section 3, we investigate which waste streams exist in connection with the PtX plants implemented so far and how the three case study PtX plants could valorize waste streams (inputs and outputs) from the electrolysis process. Further, we identify whether energy system integration is obtained within the cases and, hence, was included as an important element for the plant layout/design.

The key questions we asked, and elements we investigated within the case studies to obtain a greater understanding of how a more symbiotic PtX development could be achieved, can be outlined as follows:

- Renewable Energy Sources (RES): Where does the electricity come from?
- Carbon dioxide: Does the plant rely on CO_2 from biogenetic or non-biogenetic sources?
- Water: Where does the water for the electrolysis processes come from?
- Waste heat: Is the surplus heat being utilized?
- Oxygen: Does pure oxygen have any usage?
- Energy system integration: Is the layout/design stabilizing the fluctuating RES within the energy system?

3. Results

In this section, the results of the exploratory case study reviews are presented.

3.1. Case Presentation

In the following, we present the results of the exploratory case study investigations of the three selected PtX plants, with the aim of identifying *which* and *how* waste streams are being, or will be, valorized, as well as to *what* extent energy system integration has been included in the plant layout/design. We introduce the PtX plants by following the topics presented earlier and depict the plant configurations in Figures 2–4, respectively.

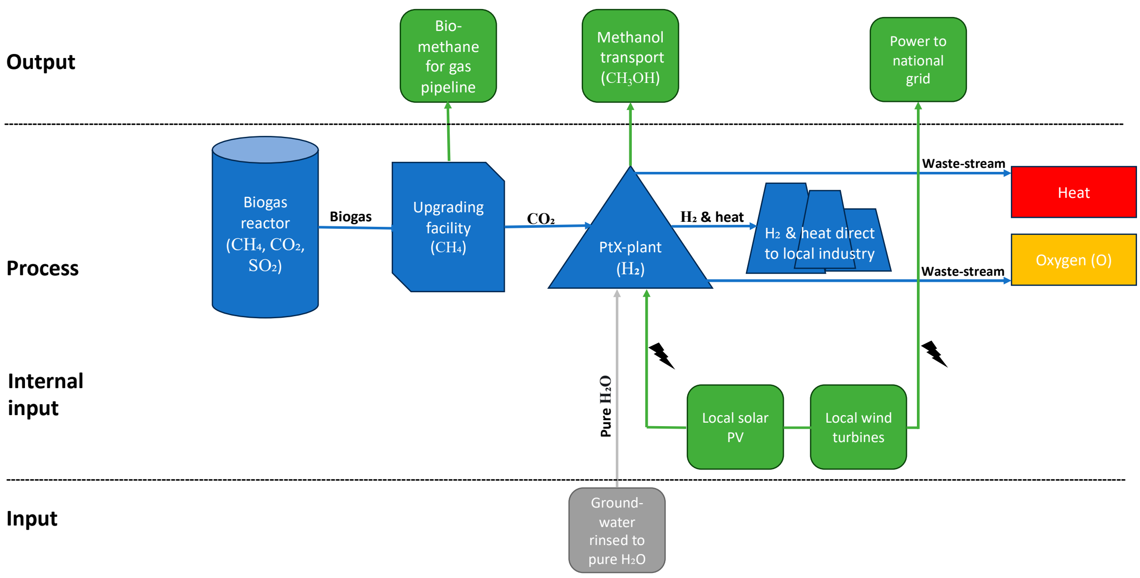

Figure 2. EnergyLab Skive and PtX plant.

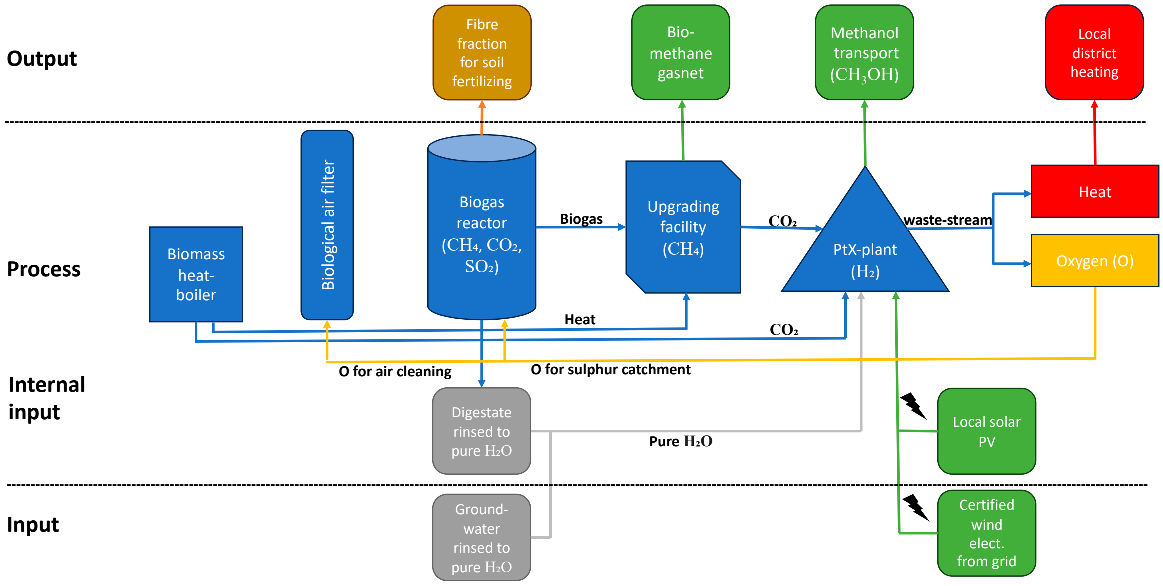

Figure 3. Vinkel Bioenergy and PtX plant.

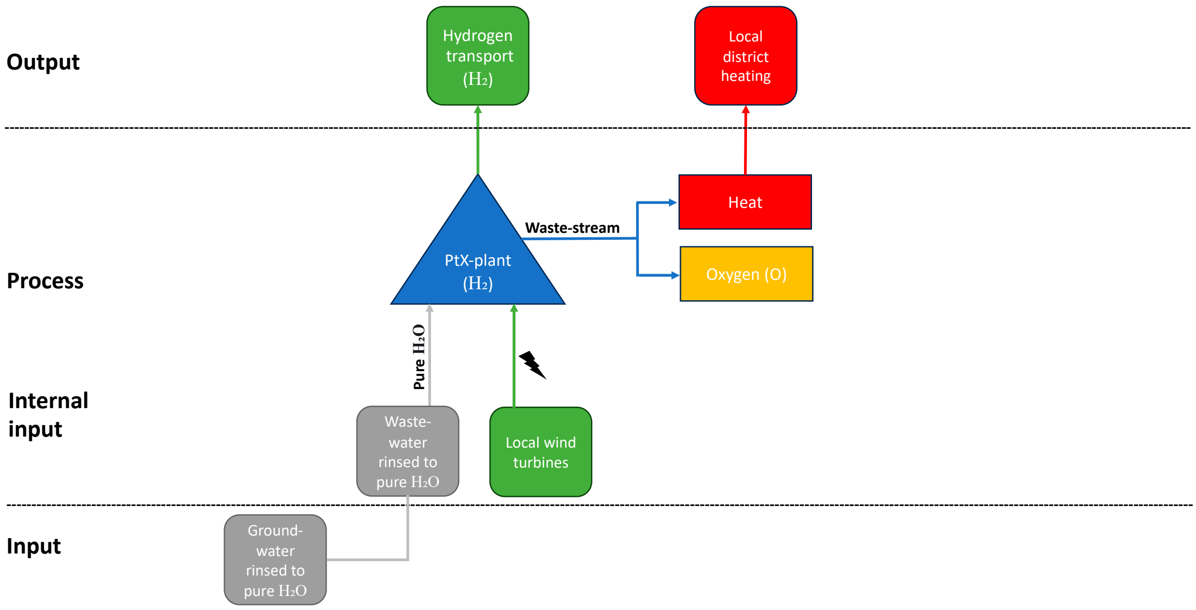

Figure 4. DIN Forsyning and PtX plant.

3.1.1. Case Study 1: EnergyLab Skive and PtX Plant (the Energy Hub Case, Figure 2)

Introduction: GreenLab Skive is a green cluster of industries that are located together to optimize the use of resources due to their proximity and based on the types of companies in the cluster. The overall target is a 120 MW PtX plant. Currently, two modules of six MW are implemented and being tested. Hydrogen pipes are distributed in the ground to supply local businesses with hydrogen for their manufacturing processes. The current operation's 12 MW electrolysis capacity in GreenLab Skive is initially producing 10 M liter methanol. Later, this will also produce ammonia for the transport sector, although the production of ammonia requires an air separation unit and nitrogen storage facility. In the future, the external storage of hydrogen will also facilitate the production of compressed hydrogen for the heavy transport sector and for industrial usage.

RES: Electricity is provided by a nearby solar PV park with a 26 MW capacity, as well as 54 MW wind turbine capacity from a total of 13 Vestas turbines. This case thus represents a hybrid RES park. Overall, 80 MW RES energy is needed to achieve a 15 MW electrolysis capacity, but with a target of 120 MW electrolysis, a considerable amount of RES must be implemented in the future. At some point, a large battery will also be implemented to store electricity from the RES production. The supply of RES to the national grid is currently an option for consideration.

CO_2 usage: Biogenetic CO_2 is captured from the on-site biogas plant's upgrading facility, amounting to around 26,500 t/y. The CO_2 is used for methanol production, whereas the hydrogen production does not require any supply of carbon.

Water: Water is supplied from groundwater resources that are polluted and not appropriate to use as drinking water. Alternatively, the desalination of water could be applied at the plant if no other water resources could be utilized.

Waste heat: The waste heat from the electrolysis process is currently not being utilized, except for minor quantities piped to local industries. The deployment of a future district heating system is being discussed as an opportunity for the local community. Up to one-third of the energy production ends up as waste heat, with a temperature of around 75 °C, which would be appropriate for district heating purposes. However, the cost of a new district heating network is DKK 500 M (EUR 67 M), meaning subsidies from the government would be required to install this or financial support from interested investors. GreenLab Skive is aiming to invite industries with a high heat demand to relocate to the site so that they can supply energy to them in the form of hydrogen from the PtX plant. Temperatures of 600 °C to 1100 °C are sometimes required by industry, which could be provided by the distribution of hydrogen to the companies. GreenLab Skive hopes to store energy in the future by storing electrons as thermal energy, like steam, and recognizes the importance of this for ensuring energy efficiency and stabilizing the fluctuating energy from RES.

Oxygen: There is no current use or future plans to use oxygen, and this output is not regarded as an important resource.

Energy system integration: GreenLab Skive is part of several projects investigating how to store heat. In the first project, the ambition is to develop an optimal design for a system that uses molten salt for heat storage and that can drive the steam supply for industrial processes. In the second project, "Energy Rocks", how to store excess electricity from wind turbines as heat in a rock bed is being investigated so that it can cover the thermal needs of GreenLab Skive and utilize the industrial park's wind and solar resources in the most optimal way. In this project, the rock bed is heated via a heater power of 60 MWel, and the target should store up to 40 MWth of energy. These projects should assist in stabilizing the fluctuating energy from RES. Thus, the thermal storage of steam, as well as the storage of hydrogen for later usage, such as in a national hydrogen pipe system or a cavern storage facility (Cluster North project), is how the PtX plant in the future can assist the stabilization of the fluctuating RES energy [49].

3.1.2. Case 2: Vinkel Bioenergy and PtX Plant ('the Rural Case', Figure 3)

Introduction: The Vinkel Bioenergy biogas plant was established in 2018 and utilizes 400,000 t of biomass feedstock annually, mainly comprising animal manure, crop residues, energy crops (maize), deep litter, and soon, also source-separated organic household waste from the city of Viborg. The plant produces 52,000 N m^3 (normal cubic meter) of biomethane annually, which is upgraded to natural gas standards and injected into the natural gas network. The PtX plant will produce methanol for the transport sector. Vinkel Biogas is currently implementing a biomass boiler (to burn residual straw and wood chips) to generate additional heat for upgrading the facility. This heat is produced from biogas today, but the energy is not sufficient.

RES: The future electricity production will rely on solar PV, and the system will be implemented on a 105 ha large land area close to the biogas plant. As a small airport is located right next to the plant, no wind turbines can be erected, and certified electricity from wind energy will be purchased instead to supplement the renewable energy production from solar. The solar PV facility will possibly be established with local ownership as a solar pool.

CO_2 usage: The PtX plant will utilize biogenetic CO_2 from the existing upgrading facility, as well as from the biomass boiler currently being implemented. The plant will thus contribute to CCU.

Water: Vinkel Biogas plans to utilize local water resources, like polluted groundwater, and rinse water (liquid manure) from the biogas process. The digested manure (digestate) contains 5–7% dry matter, which, instead, could be separated into a fiber fraction and a water fraction, and the latter could be rinsed for use in the electrolysis process. It is planned that the fiber fraction, being rich in nitrogen, phosphorus, minerals, etc., will finally be returned to farmland as valuable fertilizer.

Waste heat: The surplus heat developed from the cooling of the electrolysis process can be distributed via the district heating network for the nearby Højslev community, and from there, the heat could be distributed even further to the city of Skive. There is, hence, a large nearby heat market for excess heat. Today, 4 MW of waste heat from the cooling of the upgrading facility is lost annually. The PtX plant could make it feasible to utilize this waste heat, which could be distributed together with the PtX waste heat as district heating in the nearby network.

Oxygen: Vinkel Biogas sees several opportunities for utilizing the oxygen output from the electrolysis process. One option is to use the oxygen in the biogas reactor to catch sulfur, which is an unwanted product in biogas. Today, this oxygen is delivered via an oxygen generator that utilizes electricity from the grid. Around 100 m^3 of oxygen per hour is used to capture the content of sulfur in the biogas. Another option is to utilize the oxygen in the tower for biological air cleaning, which can be carried out by supplying oxygen that feeds the bacteria into a tower that is capable of cleaning the air. Also, in this process, around 100 m^3 of oxygen per hour would be required.

Energy system integration: The production of biogas and the distribution of biomethane to the gas network will help stabilize the energy system. This already happened before the PtX plant was established, but now, district heating will be supplied to the local community, which will assist in providing a stable energy system utilizing the already existing energy infrastructure [50].

3.1.3. Case 3: DIN Forsyning and PtX Plant ('the City Case', Figure 4)

Introduction: The PtX plant is being developed in Esbjerg harbor and produces hydrogen to fuel local boats that service the offshore industry. The plant will be established in 2023 and is owned by European Energy. DIN Forsyning, which is a municipally owned multiple distribution company (supplies water, district heating, and wastewater treatment), will be connected to the PtX plant via various services, as outlined ahead.

RES: Renewable energy produced from four wind turbines located in the community of Måde, close to Esbjerg, will be directly connected to the PtX plant and will facilitate the electrolysis process and, hence, the production of green hydrogen.

CO_2 usage: As the PtX plant will produce hydrogen only, there is no use of carbon in the process, and hence, no need for CCU technology to be connected to the process.

Water: The water usage connected with the project is high and will likely amount to around 1.5 M m^3 annually. Today, the water usage in Esbjerg city is around 3–4 M m^3 annually, so this represents a major increase in local use. It takes 13 kg of groundwater to produce 9 kg of pure water for electrolysis, which can produce 1 kg of hydrogen. Roughly 1.1 M m^3 pure water equals 1 GW electrolysis capacity; hence, the need for water is very high. DIN Forsyning will supply water—technical water—to the PtX plant, either as rinsed groundwater from alternative groundwater magazines, which are generally polluted with, e.g., pesticides or perfluorooctane sulfonic acid (PFOS), or from their wastewater treatment plants, where the dirty water is rinsed to obtain the required quality water. Groundwater for drinking water purposes is extracted from groundwater magazines that hold water that is cleaner than the ones planned to be used for the PtX plant. According to DIN Forsyning, other water resources might also be available and used as necessary.

Waste heat: The waste heat from the cooling of the electrolysis process is high, with around 20–30% of the generated energy ending up as surplus heat. The PtX plant and DIN Forsyning aim to utilize the waste heat via a district heating system, which can cover the heat usage of 200 households. Waste heat with a temperature of 70 °C will leave the PtX plant via the heat exchangers to the district heating network and return as cooling water at 40 °C. The colder return water will, hence, substitute alternative cooling processes that would otherwise have to be implemented to cool the water.

Oxygen: Currently, there are no plans for using the oxygen output from the PtX electrolysis process, but the oxygen could potentially be utilized within DIN Forsyning as oxygen in processes using aerobic microorganisms when rinsing wastewater.

Energy system integration: Sector integration is very important to ensure sustainability in PtX projects. The stabilization of the energy system can be facilitated by DIN Forsyning when operating heat pumps, electric water coolers, and heat accumulation tanks. The PtX plant in Esbjerg will, therefore, not contribute to stabilizing the energy system, but the connection to DIN Forsyning will ultimately contribute to this [41].

4. Discussion

This exploratory case study revealed large differences in how waste streams are managed and in the level of energy system integration within three different PtX plants investigated as case studies. In the following, we discuss which form of symbiotic collaboration (inter-firm, regional, or long-distance collaboration) is being achieved in these three different cases, being an energy hub case, a rural case, and a city case, respectively. How to locate forthcoming PtX plants, especially in regard to existing and future biogas plants as development drivers, is also discussed at the end of the section.

The use of waste streams within or in proximity, i.e., *inter-firm collaboration*, to the Vinkel Biogas plant and PtX plant has been highly developed, together with the valorization of the oxygen output as an input to the biogas production process and air filtering, while the digestate output from the biogas plant provides rinsed water input to the PtX plant. Besides, inter-firm collaboration is further strengthened using biogenetic CO_2 from the biogas' upgrading facility as an input in the process of producing methanol. At the GreenLab Skive and PtX plant, the use of biogenetic CO_2 is also valorized via inter-firm collaborations with the PtX plant as input to the production of methanol, just as the distribution of pipes within the hub can facilitate the use of minor quantities of heat within local companies in proximity to the PtX plant. For the case of the DIN Forsyning and PtX plant, it is merely the input of municipal wastewater, rinsed for PtX production, that displays a form of inter-firm collaboration, with no other waste streams currently being valorized within the surrounding proximity. Hence, the GreenLab Skive and PtX plant is the only case that solely relies on external water inputs from groundwater resources for the electrolysis process.

When it comes to *regional collaboration*, the exploratory case studies also showed great differences. At the GreenLab Skive and PtX plant, no heat output is provided as input to the community, and there are no expectations of any district heating systems to be deployed within the near future. Instead, future methods of storing the heat/steam outputs will eventually allow valorizing these waste streams later when opportunities are found and when a feasible technology solution to do so is available. DIN Forsyning, on the other hand, already valorizes its heat output as input to a regional district heating system and expects to include any future contributions from upscaling of the PtX plant and, hence, to utilize the excess heat in their system. The Vinkel Biogas plant and PtX plant also valorize heat output from the PtX plant as input to a larger district heating network in the region.

Long-distance collaboration for the supply of biomethane to the national gasnet is achieved by the Vinkel Biogas plant and PtX plant and the GreenLab Skive and PtX plant, but this was not initiated via the deployment of the PtX plants as this energy output was established before the electrolysis processes were even implemented. Moreover, the

GreenLab Skive and PtX plant distributes outputs of electricity to the national power grid but expects that the deployment of a large battery will help store future electricity outputs for more flexible locale usage. Further, the storage of future hydrogen outputs in pipes and caverns will provide various benefits by supporting further energy system integration. The DIN Forsyning and PtX plant does not provide inputs to such energy services, being involved only in long-distance collaborations, as its compressed hydrogen is merely produced for the offshore shipping industry. The stabilization of the fluctuating energy system is applied by DIN Forsyning; however, not in connection with the PtX plant but rather in relation to some other technical applications adopted, e.g., heat pumps and heat accumulation tanks.

The exploratory case study illustrated the existence of a wide variety of energy system integrations of the energy services produced by the PtX technology, as well as future opportunities not yet harvested. The GreenLab Skive and PtX plant is in its first development stage, which currently negatively impacts the valorization of waste streams. In time, and with extensive economic resources, the hub could illustrate many benefits as far as producing, distributing, utilizing, and storing hydrogen, as well as heat, in new systems that must be tested and developed further. The current energy system integration is yet non-existent, and fluctuating RES are simply distributed to the national power grid without having any stabilizing effect applied to them. Thus, the naming of the GreenLab Skive (Lab = laboratory) is an accurate synonym for the energy hub being developed over a long time and where the expected results are unsure.

The Vinkel Biogas plant and PtX plant case study illustrates how PtX can benefit from being co-located next to a biogas plant, and hence, this would instantly increase and help realize the valorization of many of its waste streams, both internally and externally. This has been highlighted as an important factor for plant viability in the current scientific literature. Thus, energy system integration can be provided by the supply of heat as district heating and biomethane to the already applied national gasnet. The DIN Forsyning and PtX plant also provides energy system integration via the distribution of district heating in existing systems. However, its compressed hydrogen production does not utilize any of the surplus biogenetic CO_2 that is currently emitted to the atmosphere, as in the other cases, which is a missed opportunity, and thus, its energy system integration is limited in its symbiotic outreach.

While the GreenLab Skive and PtX plant could provide important knowledge and results for assessing PtX implementation in the future, we stress the importance of relying on biogas plants as drivers for the deployment of PtX plants right now. Currently, 675,000 t of biogenetic CO_2 annually is emitted to the atmosphere from Danish biogas plants' upgrading facilities [42] and is not valorized, as described in Section 2.2.2. The theoretical potential CO_2 available until 2040 is estimated to be between 700,000–1.3 Mt of biogenetic CO_2, and when including CO_2 emitted from biomass combustion and waste incineration plants, the potential increases to between 2.4–3.4 Mt [51]. CO_2 can, however, also be extracted from atmospheric air, but the technology is still immature and, hence, costly [51]. The production of carbon-based energy carriers via electrolysis would, hence, initially benefit from being co-located next to biogas plants, where biogenetic CO_2 is available—and already being captured—which would, hence, facilitate the valorization of many other waste streams, as described.

If *methanation* is prioritized as an energy carrier system, existing biogas plants with upgrading facilities should be selected as drivers for PtX technology and suggested that such plants should normally be located near a national gasnet. Also, in situ or ex situ methanization techniques can be applied to increase the gas yield even further. PtX plants could also be co-located near biogas plants with no access or limited access to a gasnet and produce *methanol* as an energy carrier. Such biogas plants should typically be located near a district heating system that supplies heat to a community. However, methanol can also easily be transported via truck to other facilities and, hence, could be used to fuel the transport sector. In both cases, especially the first, the distribution of excess heat to a nearby heat market is pivotal to obtaining symbiosis in the production of electrolysis. Existing biogas plants, as well as the deployment of future biogas plants, could hence be planned and integrated into the PtX plant layout/design to enable the valorization of multiple waste streams and provide high integration with the existing energy system. In the case of the Vinkel Biogas plant and PtX plant, we discovered an example of a *hybrid PtX plant* layout/design, where methane, methanol, and district heating will be produced simultaneously, which might be possible in some cases depending on the energy system infrastructure, among other factors.

5. Conclusions

PtX is expected to become an important part of the European energy supply, and ambiguous political targets have been put forward to push the development of electrolysis technology. This is no different in Denmark, where 4–6 GW electrolysis capacity is expected to be deployed before 2030, and several PtX development projects have already been implemented, with several new ones also in the pipeline. This work investigated how waste streams from the electrolysis process could be valorized and create symbiotic collaborations in which resources could be utilized and not wasted and looked at where future PtX plants could be sited in proximity to already implemented technology. Three exploratory case studies were investigated (a rural case, a city case, and an energy hub case), showing very different emphases and capabilities for valorizing waste streams depending on, e.g., the type of PtX plant layout/design, the evolution stage currently reached, the energy carriers being produced, and the access to important energy infrastructure. The findings add to a current gap in the scientific literature, as stressed in, for example, refs. [20–25].

We conclude that PtX in the present development and implementation stage could benefit from co-locating next to biogas plants—as illustrated in the rural case—where upgrading facilities could provide an opportunity for the capture of biogenetic CO_2 that is currently being emitted to the atmosphere and hence lost. This applies to both hydrogen for e-fuels and hydrogen for methanation. Using biogenetic CO_2 as an input for the electrolysis processes and co-locating these plants in connection with biogas plants would enable the symbiotic usage of carbon and options for the high valorization of various waste streams, such as waste heat, oxygen, wastewater (digestate), and additional biogas yield via methanation. Energy system integration could thus immediately be achieved, as energy outputs would comply with the existing energy system, which would hence stabilize RES sources. Thus, superior internal, regional, and long-distance symbiotic collaborations could be realizable when focusing on biogas plants ('the rural case') as drivers for the current PtX development compared to in 'the city' and 'the energy hub' cases investigated.

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Appendix A. Questionnaire for Interviews

- When was the PtX plant erected/planned to be erected?
- What was the motivation for implementing the technology?
- What types of energy carriers are produced?
- Are there any public grants or the like connected to the technology deployment?

- Where do the renewable energy sources (RES) come from? Do you have your own supply of RES from wind turbines or solar PV? Others?
- From where does the water for the electrolysis processes come from? Rinsed wastewater or groundwater resources? Others?
- Does the PtX plant rely on CO_2 from biogenetic or non-biogenetic sources?
- How is waste heat being utilized, if at all? And, is this important?
- Pure oxygen outputs: Does the oxygen have any usage? Is this important?
- How does the layout/design of the PtX plant assist in stabilizing the fluctuating RES within the existing energy system?
- What are the future plans in relation to the PtX plant? To expand the production?

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