PtX-Plus: Synergies Through Coupling of PtX Facilities with a Biorefinery

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In order to meet the climate targets, both the German Federal Government's National Hydrogen Strategy and the EU Commission's Green Deal [2] rely on so-called green hydrogen. Conversion to hydrogen and chemical products (Power-to-X, PtX) is ideal for storing volatile amounts of electricity from wind and solar energy. If suitable biocatalytic facilities are added to this route, the product range can be controlled such that – under suitable boundary conditions – the production network can be operated economically, while adding value to unit operations that are already installed (Power-to-X-Plus, PtX-Plus).

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1 Green Hydrogen as a Key Factor

In an interview with the German Handelsblatt gathering much attention in February 2020 [1], Anja Karliczek, German Federal Minister of Education and Research, quoted an order of magnitude of 800 TWh per year for the gross energy to be sourced by so-called green hydrogen, i.e., hydrogen produced from renewable energy (RE) in Germany. This is as much as 32 % of the current annual gross energy consumption in the country [2]. Even with the maximum levels of efficiency of the electrolysis technology available today, an amount of RE electricity of more than 1000 TWh per year would be required for the 2040 target, i.e., more than four times the amount of electricity produced from sun radiation, wind power, biomass and other renewable sources in Germany in 2019.

These goals do not appear to be overestimated if the decarbonization of the energy industry, transport and industrial production in particular is to actually be achieved within the available time frame according to the IPCC report [3]. The "difficult third" of greenhouse gas (GHG) emissions produced by industry including its associated transport in particular is a challenge in this regard. If, for example, all steel production of 45 million t steel/ per year in Germany were to be switched to direct reduction by hydrogen to avoid about 67 million t $CO_{2,eq}$ per year of greenhouse gas emissions, approx. 2.4 million t a^{-1} of green hydrogen or 135 TWh a^{-1} of green power on average [4–6] would be required. The need for hydrogen in the transport sector in the medium term is even larger (on average 220 TWh a^{-1} until 2050) [5, 7]. This is surpassed by the EU usage potential of hydrogen for decarbonization of the chemical industry, in particular of the refineries, in all of the EU until 2030 [8]. According to a study published in 2018, it adds up to more than 8 million t a^{-1} of hydrogen and/or 400–780 TWh of RE electricity needed in this regard [9, 10]. Despite the gigantic amounts of energy and capital required in this regard, there is a lot indicative of theory becoming practice; after all, 95 % of the top managers of the chemical industry want a change in values towards more sustainable value added, according to a recent survey of CHEManager [11].

Apart from the quickly rising hydrogen demand, another aspect is that the fast expansion of renewable energy

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production capacities in the power sector and the acceleration of the transport sector's transition to electromobility are limited by a lack of capacities and expansion problems in the transport infrastructure. Therefore, the energy sector requires storage capacities to cushion the volatile yield of RE power production, for which chemical storage in the form of hydrogen and derivatives is an option. In freight traffic (trucks, freight trains, container ships, etc.), technologies based on the integrated fuel tank (hydrogen, synfuels) promise faster scaling than carrying along an energy storage device (battery) in electric vehicles.

However, sufficient hydrogen alone would not satisfy the needs to decarbonize all sectors of industry and society. Hydrogenation of carbon dioxide and other carbon sources to hydrocarbons, such as fuels and basic chemicals by means of green hydrogen, which is produced from renewables with close-to-zero GHG emissions, offers potentially attractive options to take in the energy, transport and climate policy transition. With this background, a seemingly growing interest in PtX technologies (Power-to-X = hydrogen, gas, synfuels, chemicals, etc.) can currently be observed worldwide.

2 Power-to-X – Options and Obstacles

The application of the PtX principle is prepared or already practiced in various locations in Germany (in 25 HyLand regions as hydrogen pilot regions, among others [12]). Its basis is the local availability of renewable energy generated by photovoltaics, onshore and offshore wind power or even all three sources in the best case. Therefore, PtX locations on the coast have an advantage due to the higher yield and consistency of wind and the proximity to offshore wind farms. This power is used to separate water into hydrogen (1 part by mass) and oxygen (8 parts by mass) by means of electrolyzers. The hydrogen is used directly (predominantly by means of fuel cells in transport, e.g., in public transport) or can be processed thermochemically to methane, methanol or other chemicals (predominantly synfuels = synthetic fuels) in combination with CO_2. The related technologies are well known at least for decades and mature; regarding electrolysis and fuel cells they are even market established. In this regard, the challenges of PtX are of an economic rather than a technological nature.

Even on the coast there are times in which neither the sun is shining, nor the wind is blowing. These periods are called "dark doldrums" and may constitute up to 4 % of the annual operating time [13]. The volatility of the provision of renewable energy depending on the time of day and the season is high. If the power transformer plant (electrolyzers and auxiliary plants, approx. 50 % of the investment costs of the central PtX facility according to [14]) is to be operated continuously, a back-up connection to the integrated power grid is imperative. The same applies as a consequence from the excess energy production yielded by local renewable energy sources unavoidable at certain times in the year and of the day if these excess quantities of electricity are to be fed into the power grid. Both for the quantity of electricity produced by the plant itself and for purchasing electricity from a third party, the connection to the integrated power grid has a fatal economic effect, at least according to the German energy law provisions: It means that the requirements for internal consumption of auto-produced electricity in so-called isolated operation (without connection to the integrated power grid) pursuant to the German federal energy law are no longer given, and charges (in particular the EEG reallocation charge), fees and electricity tax for the power sourced from third parties are incurred. The share of fees, charges, and electricity tax in the average price of electricity for the industry (0.1844 € kWh^{-1} [15]) was approx. 52 % in 2019, i.e., less than half of the effective price of electricity can be attributed to the costs of electricity generation, use of the power grid and power distribution.

Currently, approx. 8–10 € kg^{-1} are demanded at the few service stations offering hydrogen. Until 2030, a reduction of the price demanded by producers of hydrogen to approx. 1.8 € kg^{-1} and to less than 1 € kg^{-1} until 2050 is expected [16]. However, with current electrolyzer costs in the order of magnitude of 30 million € for 20 MW_{el} and grid power cost at the current industrial electricity price level in Germany, this is out of question, even with self-produced and internally consumed electricity for which 40 % of the EEG relocation charge must be paid due to partial feed-in into the grid. Therefore, PtX plant concepts are in a catch-22 situation: On the one hand, as much of the electricity demand as possible should be covered locally with the own RE plant, avoiding the feeding of excess electricity into the power grid if possible. On the other hand, a level of capacity utilization of the electrolyzers and downstream plants as high as possible may be achieved by means of a connection to the power grid only.

In regard to the sales of products, the conditions are also not simple by any means. Frequently, many PtX plant concepts are targeted towards the hydrogen use in the transport sector, initially towards the straightforward usage options in public transport in particular. However, a demand for hydrogen still has to be developed by retrofitting fleets and building up a service station network, with the hydrogen on offer and its demand impeding each other in a chicken and egg situation in the most unfavorable case. Therefore, the investors and operators are very interested in establishing further sources of income from (e.g., industrial) hydrogen sales.

Apart from that, the main product of electrolysis proportionally to its mass, oxygen, cannot be sold due to a lack of options for its local use in most cases and has to be released into the atmosphere. Usage options for the oxygen and the electrolyzer waste heat are also sought for.

3 Power-to-X-Plus

How can a steady sale of hydrogen with higher value added than in the transport and mobility market be achieved, if possible from the time the plant is out into operation, and how can the waste volume flow of oxygen be used reasonably? To answer these questions, researchers of the Technical University of Munich, together with colleagues from Bauhaus University Weimar and the industry, have developed an enhanced PtX plant concept (PtX-Plus, see Fig. 1) based on longtime developments for climate-friendly production of basic chemicals and raw materials from biomass (carbon fibers, polymers, additives generated from algae and yeasts, among others [17, 18]).

The basis for this were the development, feasibility and profitability studies of biochemical process chains for production of carbon fibers from algae and/or directly from CO_2 [18, 19]. As early as 2018, these efforts were mentioned and acknowledged as an industrial option for creating a globally relevant carbon sink in the IPCC-SR1.5 report of the Intergovernmental Panel on Climate Change [3], considering both the permanent and therefore sustainable immobilization of CO_2 in a solid (carbon fiber) and the combination of carbon fiber with hard rock to a new carbon fiber/stone composite material (CFS) for the purpose of substituting major CO_2 sources: steel, aluminum and armored concrete.

In PtX-Plus the classical PtX plant setup (local RE power production from a combination of wind power and PV plant, electrolyzer, hydrogen storage and filling) is complemented by two value-added process routes.

1st Additional Process Route

On the methanol PAN route, approx. 50 % of the hydrogen produced in the electrolyzer is directly converted into methanol first and subsequently into propylene, acrylonitrile, PAN fiber and finally carbon fiber. The path for this was already presented as process route 5 (Fischer-Tropsch process → methanol synthesis → methanol to propylene process (MtP) → Sohio acrylonitrile production process → PAN precursor production → carbon fiber production) in the techno-economic analysis (TEA) [18] published in 2018.

With a CO_2 price of $100\,€\,t^{-1}$ CO_2 and a hydrogen price of up to approx. $1.2\,€\,kg^{-1}$ H_2, this process route may achieve profitability. However, the CO_2 quantity needed for this is not obtained externally (e.g., by means of separated CO_2 obtained from CCS plants behind power plants) but is a waste product of the second complementary process route of yeast oil fermentation.

2nd Additional Process Route

In this process route for the production of yeast oil and subsequently possibly biofuel, bioglycerin and biomethanol, it is virtually a synergistic side effect, that part of the oxygen produced by the electrolyzer is used on the one hand, and that the CO_2 needed in the methanol PAN route is produced on the other hand.

The basis for this is the biotechnological conversion of local residual biomass (e.g., corn stover), which is turned into acetic acid as a fermentation substrate for the production of yeast oil by means of enzymatic hydrolysis. The optimized yeast fermentation process [17] uses a part of the oxygen produced by the electrolyzer, which massively increases the efficiency of this process, thus further increasing

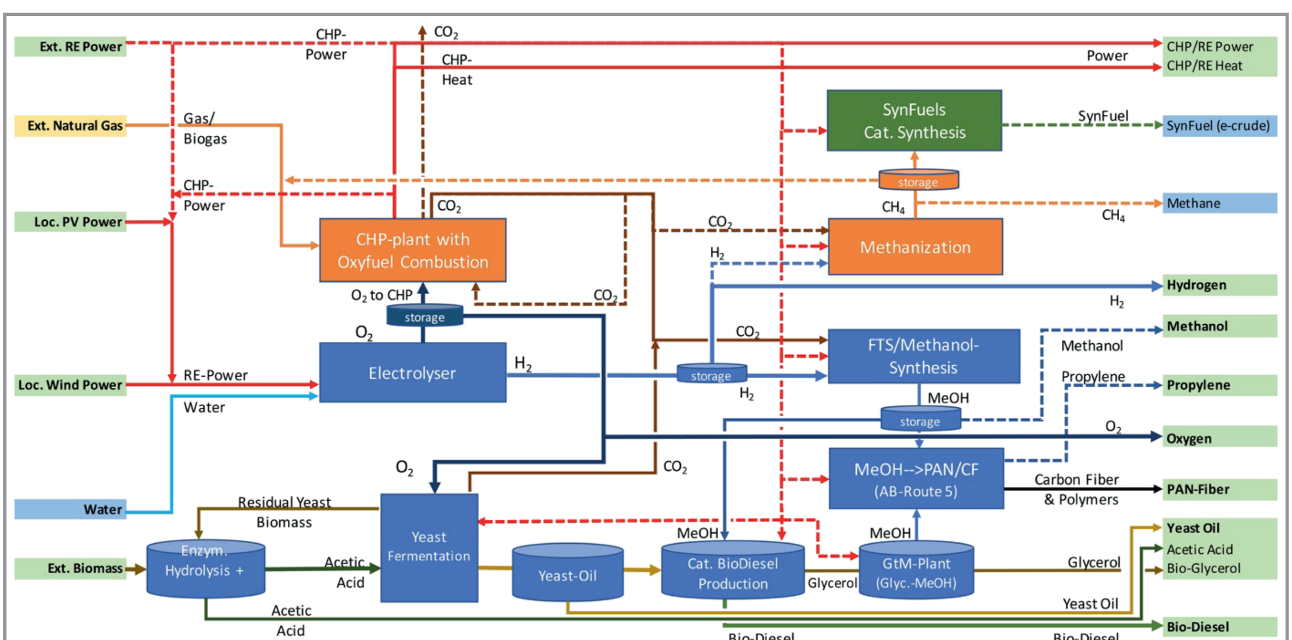

Figure 1. PtX-Plus facility layout (dotted lines: optional links, depending on specifically chosen plant and capacity configuration).

the product yield and the profitability of this process. The residual yeast biomass generated after the solvent-free oil separation is returned to the hydrolysis, significantly reducing the raw biomass needed during the process.

The yeast oil separated in the yeast reactor may, e.g., replace palm oil, which has fallen into disrepute in connection with the dramatic depletion of the rain forests. However, the yeast oil may also be processed into biodiesel and glycerin by means of a biodiesel process. The latter is converted into methanol using a glycerol-to-methanol (GtM) process and subsequently into propylene and acrylonitrile, while the purified biodiesel complements the material flow balance towards sustainable CO_2-based fuels [18].

Optional Additional Park Components and Process Routes

In order to achieve maximum flexibility of the conceptual plant compound regarding the product outlets, a natural gas based combined heat and power (CHP) plant equipped with an oxyfuel combustion process is integrated, which is able to process the remaining oxygen, delivers almost pure CO_2 as exhaust fume (usable for the Fischer Tropsch synthesis) and provides power as needed (e.g., for dark doldrums) and heat for the industrial site by means of the CHP generation. Furthermore, Fig. 1 shows the methanation of CO_2 with subsequent synfuel production (like in Herøya industrial park) as an alternative to H_2 conversion into methanol.

The innovative system solution shows how the biogenic process routes supplement the standard PtX plan and/or make it more flexible. The production capacities of the thermo- and biocatalytic PtX routes allow for significantly earlier safeguarding of the continuous site operation after start-up compared to the sole hydrogen production for the transport sector. The networked system integration presented here formidably shows the synergistic commercial and ecological effects of complementing conventional thermochemical process routes with new biotechnological procedures.

Even more diversified process routes with polymers as alternative products made from yeast oil are currently developed in the project "Green Carbon"[1)]. Yeast oil as a palm oil substitute, biodiesel as a green fuel, methanol and propylene as green basic chemicals and sustainably produced carbon fibers are possible product discharges of H_2-supported biorefinery depending on the process engineering. For a given electrolyzer capacity of 20 MW the maximum outlet capacities of renewable power (without power consumption by the electrolyzer and consecutive processes), of hydrogen, oxygen, and the different gaseous and liquid products that can be produced from the hydrogen and oxygen outlet of the electrolyzer, are displayed in Tab. 1. The most economic constellation of these product mass flows still has to be determined by optimization.

Table 1. Maximum product capacities for a given plant constellation with 20-MW electrolyzer.

Max. product capacities, alternatively (each at 100 % H_2- resp. O_2 utilization, basis: 20-MW electrolyzer	Value
Hydrogen [$Mt\,a^{-1}$]	3018
Oxygen [$Mt\,a^{-1}$]	24 141
Methane [$Mt\,a^{-1}$]	5824
Synfuel (e-crude) [$Mt\,a^{-1}$]	4476
Methanol [$Mt\,a^{-1}$]	15 164
Propylen [$Mt\,a^{-1}$]	4337
PAN fiber [$Mt\,a^{-1}$]	5039
Acetic acid [$Mt\,a^{-1}$]	151 254
Yeast oil [$Mt\,a^{-1}$]	51 080
Biodiesel [$Mt\,a^{-1}$]	42 090
Bioglycerol [$Mt\,a^{-1}$]	4291
Self-produced RE power [$MWh\,a^{-1}$]	168 040
CHP/RE power [$MWh\,a^{-1}$]	34 494
CHP/RE heat [$MWh\,a^{-1}$]	39 309

For a first and broad variation analysis of possible plant and capacity configurations of a multiproduct PtX-Plus refinery, a simplified quasi-stationary economic model was developed based upon more detailed modeling results of the authors' previous investigations (e.g., [17, 18]). The model quantifies interlinked mass and energy flows, investment and operation cost of the single process and plant components of the comprehensive PtX facility as displayed in Fig. 1. It derives the average characteristic income statement of a special purpose vehicle (project company covering investment and operation) based upon time-averaged mean values. A more detailed model description is presented in the Supporting Information (SI).

Early break-even analyses with this simplified economic model of the PtX-Plus park indicate that the hydrogen producer may run a continuous operation of its capital-intensive facilities and achieve a reduction of the hydrogen cost price to less than 2 € kg^{-1} if the oxygen is offset internally at a price of about 0.54 € kg^{-1} (which is about equivalent to that of O_2 production with an air separation plant pursuant to the Hampson-Linde cycle) and if the supply price of the offshore wind power is limited to the levelized cost of energy (LCOE). For offshore-wind power it is currently approx. 0.1 € kWh^{-1} [20].

1) Joint research project "Green Carbon", supported by the German Federal Department for Education and Research (BMBF), 2019–2022, Coordination: Technical University of Munich, WSSB.

4 Future Prospects

Compared to the classic PtX approach of hydrogen production using local RE power and subsequent use of the product in the transport sector, the expanded PtX-Plus value-added approach has the advantages of a) product diversification, b) advanced value added by producing materials of a higher value and by utilization of the oxygen byproduct, c) a higher continuity of utilization by simple transportability and usability of the intermediate products of methanol, propylene, palm oil, glycerin and possibly biodiesel in chemistry, food industry and fuel business, and d) the option to fall back onto existing capacity reserves (e.g., MtP, Sohio, PAN and carbon fiber production facilities), which may produce green products by using sustainably produced reagents in batch operation. The initial studies are promising and confirm that an in-depth examination, which also includes a careful comprehensive and dynamic TEA of the PtX-Plus facility complex and an integrated life cycle analysis (LCA), could be useful.

Outside of technological developments are the necessary adjustments of the regulatory framework in Germany (see above), which are required to grant chances of success to the desired German hydrogen strategy and industrial PtX and PtX-Plus applications.

Supporting Information

Supporting Information for this article can be found under DOI: https://doi.org/10.1002/cite.202000114. This section includes additional references to primary literature relevant for this research [21–24].

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