Optimized Multimodal Energy Systems: Integrating Proton Exchange Membrane Electrolysis and Methanol Autarky for Wastewater Treatment Plant Defossilization

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Abstract:

Defossilizing wastewater treatment plants (WWTPs) is an interesting use case for integrated energy systems that combine renewable electricity with sustainable CO_2 utilization. This study presents a literature-informed mixed-integer linear programming (MILP) framework to optimize energy procurement, asset sizing, and the operation of Power-to-X (PtX) technologies and thermal integration at a representative German WWTP. Proton exchange membrane (PEM) electrolyser performance parameters are derived from published experimental data and validated against literature ranges, eliminating the need for dedicated process simulation. Biogenic CO_2 from on-site biogas upgrading is used for methanol synthesis, while PEM electrolysis supplies hydrogen and oxygen, enabling decarbonization and sector coupling across power, heat, and hydrogen systems. The MILP model performs techno-economic optimization at 15-minute resolution over one calendar year, considering German grid regulations, CAPEX and OPEX, and investment options including PEM electrolysers, methanol synthesis, seasonal storage, photovoltaic generation, and district heating export.

Two scenarios are evaluated: a Baseline scenario representing conventional WWTP operation, and a methanol autarky scenario with full PtX integration. Results demonstrate that the methanol autarky scenario achieves complete methanol self-sufficiency and significant sector coupling at a 21 % net cost premium over the Baseline, with district heating revenue (1,076 kEUR/a) and avoided methanol purchases (544 kEUR/a) largely offsetting the 1,344 kEUR/a annualized CAPEX.

The optimized system includes a 2 MW_e PV contributing 2.3 GWh/a on-site generation. Sensitivity analysis via full MILP re-optimization reveals that both a 50 % increase and a -30 % decrease in day-ahead electricity prices raise costs by more than 200 %, underscoring the critical role of electricity procurement strategy. System-boundary carbon analysis identifies a trade-off: while scope 2 emissions increase due to higher grid consumption, the biogenic carbon loop and district heating displacement of natural gas provide substantial emission credits, with carbon parity projected at grid factors below 233 g_{CO2}/kWh.

Keywords:

Defossilization, Energy Autarky, Power-to-X, Wastewater Treatment, MILP Optimization, PEM Electrolysis, Methanol Synthesis

1. Introduction

Wastewater treatment plants (WWTPs) are critical municipal infrastructures that ensure public health and environmental protection, yet their energy intensity poses a significant challenge in the context of climate change mitigation. Across the European Union, WWTPs collectively consume between 1 % and 3 % of national electricity generation [1], making them among the largest single-site municipal energy consumers. A typical large-scale German WWTP serving several hundred thousand population equivalents requires in the order of 20 – 25 GWh of electricity annually for mechanical screening, biological treatment, aeration, sludge digestion, and tertiary filtration [2]. Simultaneously, the anaerobic digestion of sewage sludge produces biogas containing 35 – 45 % biogenic CO_2 by volume — a carbon source that, rather than being vented to the atmosphere, might serve as feedstock for the chemical industry or synthetic fuel production [3]. This dual characteristic — high energy demand coupled with biogenic carbon point source availability — positions WWTPs as particularly attractive sites for Power-to-X integration and shows potential for sector coupling. Schüth and Schunk [4] highlight the imperative of transitioning the chemical industry toward net-zero CO_2 emissions, identifying green hydrogen and CO_2-derived fuels as key enablers. Mühlbauer et al. [5] provide a portfolio-perspective assessment of carbon dioxide removal technologies and their economic potential, further motivating the utilization of biogenic CO_2 streams in industrial settings. Olah et al. [6] provide the conceptual foundation for methanol as a versatile energy carrier. Bianchi et al. [7] conclude that methanol offers favorable energy density and infrastructure compatibility among PtX routes. The exothermic methanol synthesis reaction provides process heat at temperatures above 200 °C that can be utilized within the WWTP, minimizing external heat input through systematic internal heat recovery — a concept directly relevant to WWTP integration where waste heat streams are available from both electrolysis and Combined Heat and Power (CHP) operation. Methanol is additionally required on-site at WWTPs as an external carbon source for denitrification, which makes internal production particularly attractive. On the optimization side, mixed-integer linear programming (MILP) has emerged as the standard methodology for simultaneously sizing and dispatching multi-carrier energy systems. Höttecke [8] presents an extensive multi-modal energy system design framework for industrial energy system optimization. Its application to brewery energy systems [9] provides a methodological foundation directly transferable to the WWTP context, where similar complex interactions among electricity, heat, gas, and chemical product streams must be optimized. Despite these advances, a research gap persists: No existing study integrates literature-derived PEM electrolyser parameters with a system-level MILP optimization for WWTP defossilization. Existing PtX integration studies typically rely on static efficiency assumptions for the electrolyser. Furthermore, the potential of seasonal methanol storage as a flexibility mechanism for WWTPs remains unexplored in the literature, as does the systematic valorization of electrolyzer by-products (oxygen for aeration, and waste heat for low temperature district heating) within an exergy-based framework. This paper addresses the identified gap by presenting a literature-informed MILP optimization framework. PEM electrolyser performance parameters — including specific energy consumption and thermal output characteristics — are derived from published experimental data [10, 11] and validated against established literature ranges. These parameters feed into a MILP techno-economic optimization that determines optimal asset sizing and dispatch for the entire WWTP energy system over a full year at 15-minute resolution. The methodology is demonstrated on a municipal WWTP case study, comparing a conventional Baseline scenario against a methanol autarky scenario with seasonal methanol storage, on-site methanol synthesis, oxygen co-utilization, and district heating export. The methanol synthesis efficiency is based on values reported in the literature [12], and an output composition of 50 % methanol and 50 % water is assumed. The German legal framework on wastewater discharge is applicable, specifically the Abwasserverordnung (AbwV) under federal law, with an alternative, time-limited provision in force from 1 May to 31 October. This regulatory context explains the seasonal variation in methanol demand for denitrification — not primarily as a function of ambient temperature, but due to legally prescribed discharge parameters [13].

The paper is organized as follows: Section 2 details the methodology, Section 3 describes the case study, Section 4 presents and discusses the results, and Section 5 summarizes the conclusions.

2. Methodology

2.1. System Description

The optimization framework considers a multi-carrier energy system at a municipal WWTP. The system boundary encompasses electricity procurement (grid import, CHP generation, photovoltaic potential), hydrogen production via PEM electrolysis, methanol synthesis from biogenic CO_2 and green hydrogen, seasonal methanol storage, oxygen co-utilization for biological aeration, and district heating export from waste heat recovery. The modelled energy carriers include electricity, low-temperature heat, high-temperature heat, hydrogen, oxygen, carbon dioxide, methanol, and sewage gas.

2.2. MILP Techno-Economic Optimization

The methodology employs a multi-modal energy system design framework [9], a MILP-based optimization tool that simultaneously determines optimal asset sizing and energy dispatch across multiple carriers. The optimization horizon spans 8,760 hours (one full calendar year) at 15-minute time-step resolution, yielding 35,040 decision epochs. The modelled energy carriers include electricity, low-temperature heat, high-temperature heat, hydrogen, oxygen, carbon dioxide, methanol, and sewage gas. The objective function minimizes the total annualized expenditure (TOTEX):

$$\min TOTEX = \min \sum_i AF \cdot CAPEX_i + \sum_j \sum_t c_{j,t} \cdot E_{j,t} - \sum_k \sum_t r_{k,t} \cdot E_{k,t} \tag{1}$$

where $CAPEX_i$ is the investment cost of asset i, AF is the annuity factor computed from a 20-year asset lifetime and the weighted average cost of capital (WACC), $c_{j,t}$ and $E_{j,t}$ denote the time-resolved unit cost and energy consumption of commodity j at time step t, and $r_{k,t}$ and $E_{k,t}$ represent the revenue rate and export quantity of product k. The annuity factor is defined as:

$$AF = \frac{WACC^n \ (WACC - 1)}{WACC^n \ - 1} \tag{2}$$

where n is the economic lifetime in years. The decision variables encompass continuous variables for asset capacities (electrolyser rating, methanol synthesis throughput, CHP capacity, tank volumes, district heating connection capacity, grid connection capacity) and time-indexed dispatch variables (grid purchase and sale, CHP electrical and thermal loading, electrolyzer setpoint, methanol production rate, storage charge and discharge rates). Binary variables are employed for unit commitment of dispatchable assets, ensuring that minimum up-time and down-time constraints are respected.

Constraints enforce energy balance closure for each carrier at every time step:

$$\sum_i generation_{i.t} - \sum_{ji} demand_{j.t} - \sum_k storage\ charge_{k.t} + \sum_i storage\ discharge_{k.t} = 0, \quad \forall t \tag{3}$$

Additional constraints include storage dynamics (state-of-charge evolution, maximum charge/discharge rates, and cyclic boundary conditions ensuring identical start and end states for seasonal storage), German grid regulatory requirements (power purchase agreements, grid connection limits at the point of common coupling), and the linearized electrolyser performance. The methanol synthesis is modelled as a linear conversion of H_2 and CO_2 feedstocks with fixed stoichiometric ratios (1 mol CO_2 + 3 mol H_2 → 1 mol CH_3OH + 1 mol H_2O) and a linearized heat balance for the exothermic reaction.

3. Case Study

The case study considers a representative large-scale German municipal WWTP with an annual electricity demand of approximately 20 GWh/a, distributed across mechanical cleaning (screening, grit removal), primary and secondary biological treatment (activated sludge aeration, nitrification, denitrification), anaerobic sludge digestion, tertiary sand filtration, ultraviolet disinfection, and administrative facilities. The plant's biogas production from anaerobic digestion amounts to approximately 8,304 t/a, with a methane content of 60 – 65 % by volume, corresponding to an energy content sufficient to fuel the existing CHP fleet. The existing CHP fleet comprises two 500 kW_{el} units and two 800 kW_{el} units (total 2,600 kW_{el}). After biogas upgrading via pressure swing adsorption and membrane separation, the biogenic CO_2 stream is available at sufficient purity for methanol synthesis. The hourly load profiles for electricity demand, biogas production, and heat demand are derived from twelve months of operational monitoring data and exhibit typical diurnal and seasonal patterns, with peak electricity demand during daytime aeration cycles and elevated heat demand in winter months.

3.1. Scenario Definition

Scenario A — Baseline: The WWTP operates conventionally without PtX integration. Electricity is supplied by the existing CHP units and grid imports. Methanol for internal use (denitrification carbon source, approximately 1,000 t/a) and oxygen for aeration are purchased from external suppliers at market prices. No district heating export occurs, and all CHP waste heat beyond internal demand is dissipated via cooling towers. This scenario represents the status quo against which PtX integration benefits are measured.

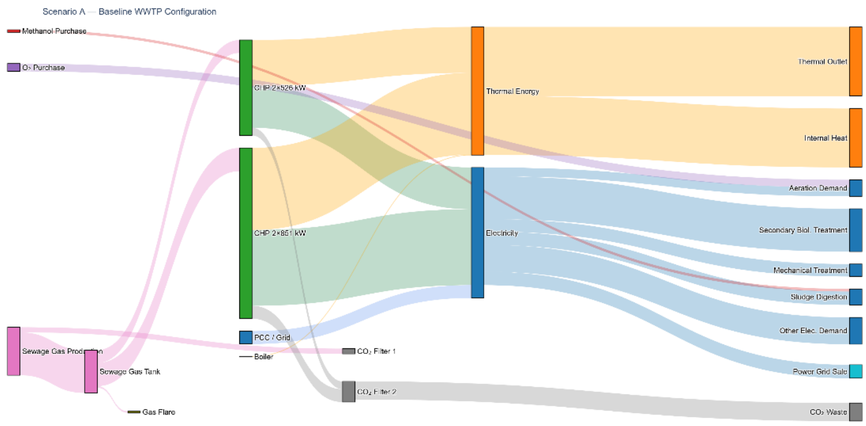

Figure 1. Sankey diagram of annual energy and mass flows — Baseline scenario.

Scenario B — Methanol autarky Seasonal: Full PtX integration is implemented. A PEM electrolyzer produces hydrogen, which is combined with biogenic CO_2 in an on-site methanol synthesis reactor (656 kWh_e per ton of methanol [12]). A seasonal methanol storage tank buffers mismatches between production and consumption. Electrolyzer-produced O_2 is co-utilized for aeration, reducing external oxygen procurement. Waste heat from the electrolyzer and a new CHP unit (CHP_{NEW}) is exported via a district heating connection to a nearby residential heat network. The optimization determines all asset sizes and dispatch schedules simultaneously. Methanol dosing follows a seasonal profile based on the Abwasserverordnung (German wastewater discharge ordinance) [13].

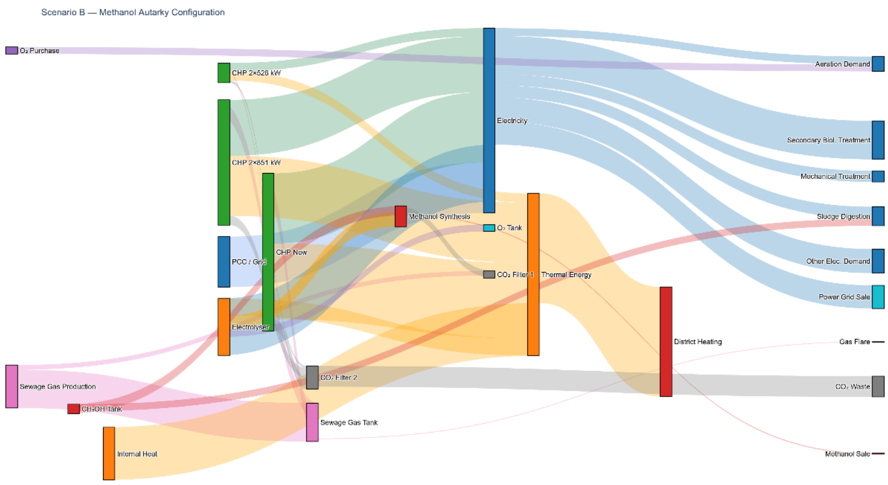

Figure 2. Sankey diagram of annual energy and mass flows — methanol autarky scenario.

3.2. Input Data and Economic Assumptions

The economic analysis employs German day-ahead electricity market prices from 2024, reflecting the hourly price volatility characteristic of markets with high renewable penetration [14]. Power purchase agreement (PPA) structures are modelled for long-term electricity procurement. Capital costs are annualized using an annuity factor (Eq. 2) derived from a 20-year asset lifetime and a project-specific WACC of 7 %. Key commodity prices include oxygen at 0.25 EUR/kg [15], methanol purchase price based on European spot market indices (460 EUR per ton MeOH [16]), and a district heating tariff based on local heat network conditions and municipal agreements. Investment costs for the PEM electrolyser (approximately 70 EUR/(kg_{H2} h) installed capacity), the methanol synthesis unit, storage tanks, and CHP units are based on current manufacturer quotations, tender documents, and published literature values [17, 18]. Grid connection charges at the point of common coupling (PCC) follow the applicable German regulatory framework for large industrial consumers and time-of-use tariffs.

4. Results and Discussion

4.1. Optimal Asset Sizing

The MILP optimization yields the asset portfolio shown in Table 1. The PEM electrolyser is sized at 119.5 kg_{H2}/h, corresponding to an installed electrical capacity of approximately 6.0 MW_{el} and requiring an investment of 8.37 MEUR — the single largest capital expenditure item, representing 59 % of total investment. The methanol synthesis reactor is sized at 632 kg_{MeOH}/h (2.73 MEUR), matched to the available biogenic CO_2 supply and hydrogen production capacity. A new CHP unit (CHP_{NEW}) of 1,979 kW_{el} (1.78 MEUR) is installed to provide both additional electricity for the electrolyser and thermal energy for district heating. The methanol storage tank capacity of 100 t (150 kEUR) enables seasonal buffering, while the district heating connection is rated at 6,650 kW_{th}. The total investment amounts to 14.24 MEUR. The optimizer selects a 2 MW photovoltaic installation (1,200 kEUR, 8.4 % of total investment) with 1,132 full-load hours, generating 2,264 MWh/a of on-site renewable electricity. This PV capacity reduces peak grid import by providing daytime self-consumption, thereby lowering PCC demand charges which constitute the second-largest cost item (2,248 kEUR/a). The relatively modest tank investment (1.1 % of the total) highlights that seasonal storage is enabled primarily by the tank volume, rather than by expensive process equipment, making it an economically efficient flexibility option.

Table 1. Optimal asset sizing for the methanol autarky scenario

Asset	**Capacity**	**Unit**	**Investment [kEUR]**
PEM Electrolyser	119.5	kg_{H2}/h	8,365
Methanol Synthesis	632	kg_{MeOH}/h	2,732
CHP_{NEW}	1,979	kW_{el}	1,781
PV	2,000	kW	1,200
CH_3OH Tank	100	t	150
O_2 Tank	57	t	—
CO_2 Tank	2,418	kg	13
District Heating	6,650	kW_{th}	—
Power Grid Connection	8,353	kW	—
CO_2 Filter 1	3,500	kg/h	—
CO_2 Filter 2	2,203	kg/h	—
Total			**14,241**

4.2. Energy Balance and Sector Coupling

Table 2 summarizes the annual energy and mass flows for the methanol autarky scenario. Grid electricity purchases increase from 4.6 GWh/a in the Baseline to 29.3 GWh/a, driven predominantly by the electrolyser's 27.8 GWh/a electricity consumption. However, this increase is substantially offset by on-site electricity generation from the new CHP unit (CHP_{NEW}), which produces 12.6 GWh/a, and by increased grid electricity sales of 5.6 GWh/a — approximately doubling compared to the Baseline level of 0.5 GWh/a. The power grid connection is expanded to 8,353 kW to accommodate bidirectional power flows.

The electrolyser produces 556 t/a of hydrogen and 695 t/a of oxygen as a co-product. The oxygen co-utilization displaces approximately 21 % of the externally purchased oxygen for biological aeration (695 t out of a total demand of 3,277 t/a), reducing O_2 procurement costs by 174 kEUR/a. Hydrogen is entirely consumed by the methanol synthesis reactor, which produces 2,943 t/a of methanol while consuming 4,044 t/a of biogenic CO_2 — equivalent to a substantial share of the available biogenic CO_2 from biogas upgrading (5,141 t/a).

The methanol storage tank operates with 9.1 charge/discharge cycles per year, confirming its role as a seasonal storage asset that buffers the mismatch between relatively steady methanol production and seasonally varying demand. The electrolyser operates for 4,875 h/a with 4,654 equivalent full-load hours (FLH), indicating significant part-load operation and off-times driven by electricity price optimization. The methanol synthesis achieves 4,654 FLH, closely tracking the electrolyser operation as expected given the direct coupling via hydrogen supply.

Table 2. Annual energy and mass balance — methanol autarky scenario.

Stream	Value	Unit
Grid electricity purchase	29,311	MWh/a
Electrolyser electricity demand	27,810	MWh/a
CHP_{NEW} electricity production	12,638	MWh/a
PV electricity production	2,264	MWh/a
Grid electricity sale	5,552	MWh/a
District heating export	26,892	MWh_{th}/a
Electrolyser H_2 production	556	t/a
Electrolyser O_2 utilized	695	t/a
Electrolyser thermal output	8,343	MWh_{th}/a
MeOH synthesis production	2,943	t/a
CO_2 consumed (MeOH synthesis)	4,044	t/a
CH_3OH tank cycles	9.1	cycles/a
Total methanol demand	2,364	t/a
External O_2 purchased	2,582	t/a
Electrolyser O_2 for aeration	695	t/a (~21 %)
Excess MeOH sold	579	t/a

The district heating export of 26.9 GWh_{th}/a represents the most significant sector coupling achievement and the primary driver of project economics. This thermal energy is sourced from the electrolyser waste heat (8.34 GWh_{th}/a at 60 – 80 °C) and, predominantly, from the new CHP unit's thermal output (approximately 13.6 GWh_{th}/a from exhaust gas heat recovery and engine jacket cooling). The district heating connection rated at 6,650 kW_{th} operates for 8,645 h/a, providing a reliable thermal supply to the local residential heat network primarily during the heating season from October to April. Table 3 presents the asset utilization metrics across both scenarios.

Table 3. Asset operation comparison — Baseline vs. methanol autarky scenario.

Asset	Baseline [FLH]	methanol autarky [FLH]
Power Grid	1,324	3,509
BHKW 2 × 500 kW	8,054	2,607
BHKW 2 × 800 kW	8,659	7,807
CHP_{NEW} (1,979 kW)	—	6,386
PV	—	1,132
PEM Electrolyser	—	4,654 (4,875 h operating)
Methanol Synthesis	—	4,654
CH_3OH Tank	—	800 (9.1 cyc/a)
District Heating	—	8,645
Gasflare	205	41 (−80%)

The CHP_{NEW} (6,386 FLH) displaces the smaller CHP units (2×500 kW, FLH dropping from 8,054 to 2,607) in the merit order, while the larger units (2×800 kW, 7,807 FLH) maintain high utilization.

4.3. Economic Analysis

Table 4 presents the comprehensive cost comparison between the Baseline and methanol autarky scenarios. The Baseline gross TOTEX is 2,735 kEUR/a (entirely OPEX), while the methanol autarky scenario has a gross TOTEX of 4,814 kEUR/a (CAPEX of 1,344 kEUR/a plus OPEX of 3,470 kEUR/a). However, the methanol autarky scenario also generates substantial revenues.

Table 4. Economic comparison — Baseline vs. methanol autarky scenario.

Cost / Revenue Item	Baseline [kEUR/a]	MeOH Autarky [kEUR/a]
Grid electricity cost	420	2,003
Grid connection charges (PCC)	869	2,248
Methanol purchase (460 EUR/t)	544	0
O_2 purchase	819	645
Oil purchase	5	3
CO_2 filter maintenance	100	100
PV CAPEX	0	113
CAPEX (annualized, excl. PV)	0	1,231
Gross TOTEX	**2,735**	**4,814**
Grid sale revenue	–22	–222
District heating revenue	0	–1,076
Methanol sale revenue	0	–232
Total revenues	–22	–1,530
Net cost (TOTEX – revenues)	**2,713**	**3,285**
Net cost change	—	**+21%**

The revenue analysis reveals the economic rationale for PtX integration. District heating export generates 1,076 kEUR/a — the single largest revenue stream. Combined with avoided methanol purchases (544 kEUR/a), these offsets together exceed the annualized CAPEX of 1,344 kEUR/a. Grid electricity sales increase from 22 kEUR/a to 222 kEUR/a, reflecting the enhanced ability to sell electricity during high-price periods through the expanded CHP fleet and optimized dispatch. Methanol purchases are entirely eliminated, saving 544 kEUR/a — this represents the core autarky achievement. Oxygen procurement costs decrease by 174 kEUR/a (from 819 to 645 kEUR/a) due to the 21 % displacement by electrolyser O_2. The net cost comparison yields a Baseline net cost of 2,713 kEUR/a versus a methanol autarky net cost of 3,285 kEUR/a — an increase of 21 %. The annual defossilization premium is 572 kEUR/a (+21 %), representing the cost of achieving methanol autarky, sector coupling, and biogenic carbon utilization. Based on gross revenue generation of 1,530 kEUR/a against an investment of 14,241 kEUR, the revenue payback period is 9.3 years.

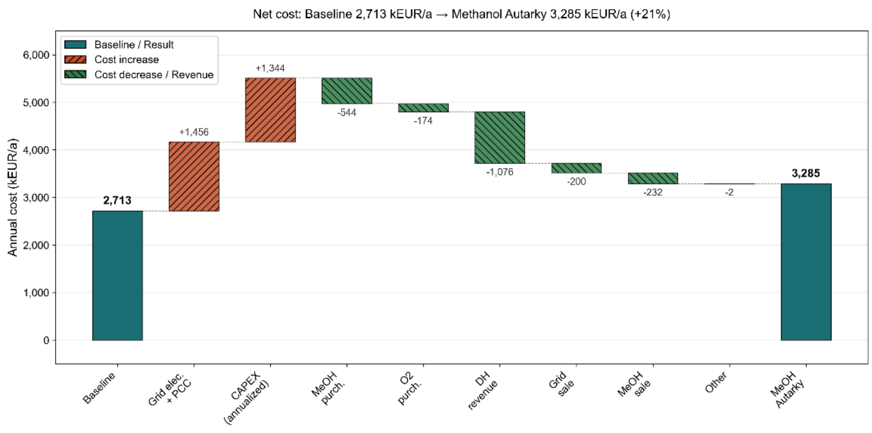

Figure 3. OPEX waterfall chart comparing Baseline and methanol autarky scenarios.

4.4. Sensitivity Analysis

A sensitivity analysis based on full MILP re-optimization was conducted to assess the robustness of the methanol autarky scenario's economic performance. Figure 4 presents the sensitivity results comparing the baseline against two day-ahead electricity price scenarios: a + 50 % increase and a – 30 % decrease. Unlike parametric sensitivity studies, each scenario triggers a full re-optimization of the asset portfolio and dispatch strategy. The base case MeOH Autarky scenario (14.2 MEUR investment) achieves a net cost of 3,285 kEUR/a. Both electricity price perturbations cause dramatic cost increases: the DA + 50 % scenario yields 10,726 kEUR/a (+ 226 %) and the DA – 30 % scenario yields 10,952 kEUR/a (+234%), despite the optimizer adding wind PPA capacity (~ 14.5 MW), lithium-ion battery storage (~ 5.3 MW), and expanding the new CHP unit from 1,979 to ~ 3,400 kW. Total investment increases from 14.2 to 19.8 MEUR in both cases. The cost breakdown (Figure 4, right panel) reveals that grid electricity and PCC charges dominate, tripling relative to the base case. The appearance of Wind PPA costs (1.7 MEUR/a) in the sensitivity scenarios reflects the optimizer procuring dedicated renewable electricity to hedge against unfavorable grid prices. The district heating tariff is the third most influential parameter, confirming the critical dependence on heat off-take revenue.

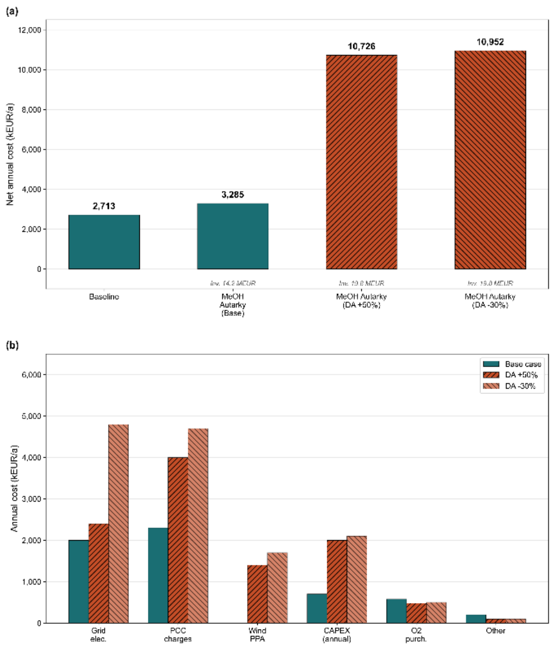

Figure 4. Electricity price sensitivity analysis: net annual cost comparison (a) and cost breakdown (b) across base case and day-ahead price scenarios (+ 50 % and – 30 %).

A key finding is that the system design is highly sensitive to electricity market conditions: both higher and lower day-ahead prices degrade the economic case, as the optimizer compensates by investing in expensive on-site generation and storage assets. This underscores the importance of stable, long-term electricity procurement (e.g., PPAs) for PtX project viability. The base case achieves the most favorable outcome because the existing 2024 day-ahead price profile provides sufficient low-price hours for cost-effective electrolyser operation without requiring dedicated renewable procurement. The Baseline net cost of 2,713 kEUR/a provides the reference for evaluating defossilization costs: the base case MeOH Autarky premium is 572 kEUR/a (+ 21 %), representing the annual cost of achieving methanol autarky and sector coupling. Figure 5 illustrates the underlying price duration curves and resulting grid-import patterns that drive these re-optimization outcomes

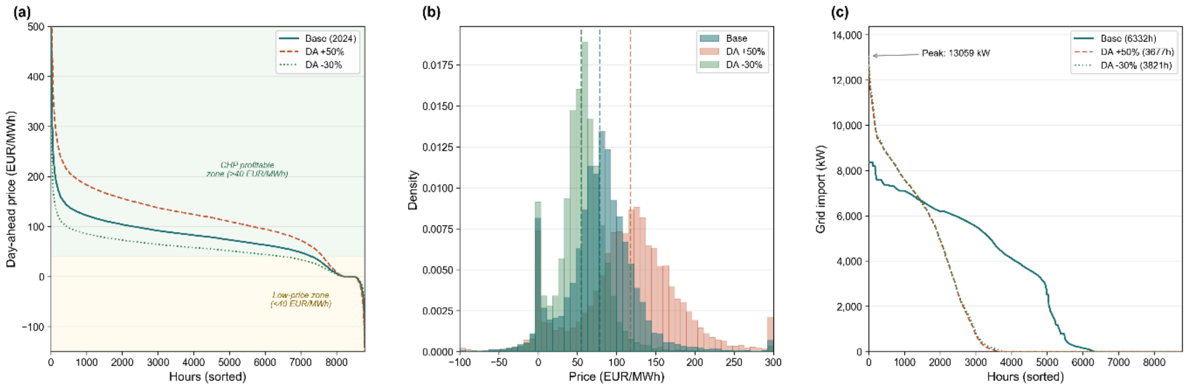

Figure 5. Day-ahead electricity price duration curves (a), price distribution (b), and resulting grid import duration curves from MILP optimization (c), illustrating the sensitivity of system design to price profile shape.

4.5. Carbon Emissions Analysis

The transition to the methanol autarky scenario fundamentally alters the carbon footprint profile. The following analysis considers scope 2 operational emissions based on grid electricity consumption. It does not constitute a full life-cycle assessment (LCA) and excludes embodied emissions from equipment manufacturing, construction, and catalyst degradation. Direct scope 2 emissions increase from 1,466 t CO_2/a (Baseline) to 9,409 t CO_2/a due to 6.4 times higher grid electricity consumption, applying the German grid emission factor of 320 g CO_2/kWh [19].

Two system-boundary emission credits partially offset this increase. First, the biogenic carbon loop: sewage gas CO_2 is captured, fed through the CO_2 tank into the methanol synthesis reactor, and converted to methanol for on-site denitrification. This displaces 1,182 t/a of externally purchased fossil methanol, avoiding an estimated 544 t CO2/a in upstream fossil methanol production emissions. Second, the district heating export of 26.9 GWh_{th}/a — sourced from CHP waste heat and electrolyser thermal output, both ultimately derived from biogenic sewage gas combustion — displaces natural gas boilers in the connected residential heating network, avoiding approximately 4,831 t CO_2/a (at 180 g CO_2/kWh for natural gas heating).

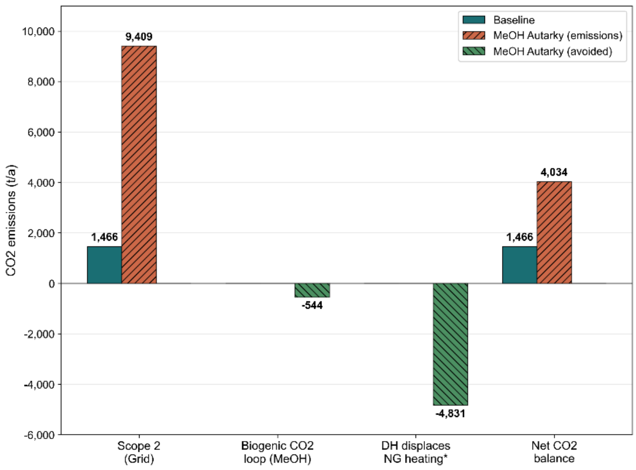

Figure 6. CO_2 emissions comparison: Scope 2 emissions and system-boundary credits for Baseline and methanol autarky scenarios.

The net system-boundary CO_2 balance yields the following result: Baseline 1,466 t CO_2/a versus methanol autarky 4,034 t CO_2/a. While the methanol autarky scenario has higher net emissions under current grid conditions, this trade-off will diminish as the German electricity grid continues to decarbonize. At a grid emission factor below 233 g CO_2/kWh — projected to be reached before 2030 under current expansion targets — the methanol autarky scenario would achieve carbon parity with the Baseline.

4.6. Exergy Analysis and Efficiency Gains

The exergy analysis provides the thermodynamic foundation for the system design and identifies the key drivers of efficiency improvement. The electrolyser's waste heat output of 8.34 GWh_{th}/a, produced at temperatures suitable for low-temperature district heating (60 – 80°C supply temperature), represents recoverable thermal exergy that would be destroyed in a conventional air-cooled or water-cooled rejection system. At a mean source temperature of 70 °C and a reference temperature of 10 °C, the Carnot factor is approximately 0.175, yielding a thermal exergy recovery of roughly 1,460 MWh_{ex}/a from the electrolyser alone.

The CHP_{NEW} contributes approximately 13.6 GWh_{th}/a of waste heat from exhaust gas heat recovery and engine jacket cooling at higher temperatures (80–120 °C), constituting the dominant thermal source for the district heating network. Together with supplementary heat from the existing CHP fleet and the methanol synthesis exotherm, these sources enable the 26.9 GWh_{th}/a district heating export. The total thermal exergy recovered for useful purposes — rather than being dissipated — demonstrates the practical value of exergy analysis in guiding system design: without this thermodynamic evaluation, the district heating connection would likely have been undersized or omitted, thereby forgoing the dominant revenue stream.

The chemical exergy analysis reveals the thermodynamic value of the product transformation pathway. Hydrogen produced by electrolysis has a lower heating value (LHV) of approximately 120 MJ/kg, while the methanol product has an LHV of approximately 20 MJ/kg. Despite this apparent energy density reduction on a mass basis, the conversion is thermodynamically justified because methanol offers superior volumetric storage characteristics (liquid at ambient conditions, density ~792 kg/m³ vs. compressed H_2 at 20 kg/m³ at 350 bar) and directly displaces a fossil-derived product used in the WWTP. The CO_2 consumed in the synthesis (4,044 t/a) represents biogenic carbon that would otherwise be emitted as a greenhouse gas, providing a carbon utilization pathway aligned with circular economy principles and the EU Taxonomy [6, 20].

The oxygen co-utilization merits particular attention from an exergy perspective. Conventional oxygen production via the Linde (cryogenic air separation) process requires approximately 0.35 kWh_{el}/kg_{O2} [21,22]. By utilizing the 695 t/a of electrolyser-produced oxygen for wastewater aeration, the system avoids approximately 243 MWh_{el}/a of embodied electrical exergy destruction in the displaced oxygen production process. While modest in absolute terms, this co-utilization illustrates the principle that by-product valorization at PtX sites can improve overall system exergy efficiency without additional capital investment.

5. Conclusions

This study presents a literature-informed MILP optimization framework for the defossilization of wastewater treatment plants through integrated Power-to-X technologies. The methodology combines published PEM electrolyser performance data with system-level techno-economic optimization at 15-minute resolution to determine optimal asset sizing and dispatch for a representative German WWTP.

The key findings are as follows:

(1) The methanol autarky scenario achieves methanol autarky and sector coupling at a net cost premium of 21 % (from 2,713 to 3,285 kEUR/a) compared to the Baseline, on a total investment of 14.24 MEUR. District heating export (1,076 kEUR/a) and eliminated methanol purchases (544 kEUR/a) are the dominant economic offsets, together exceeding the annualized CAPEX (1,344 kEUR/a).

(2) Sensitivity analysis via full MILP re-optimization reveals that electricity price is the critical parameter: both +50% and −30% day-ahead price scenarios increase net costs by over 200%, driven by asymmetric mechanisms (added hedging CAPEX under high prices; collapsed export revenue under low prices). The base-case Methanol Autarky premium over the Baseline is 572 kEUR/a (+21%), a manageable defossilization cost.

(3) System-boundary carbon analysis reveals a trade-off: direct scope 2 emissions increase from 1,466 to 9,409 t CO_2/a due to higher grid consumption, partially offset by the biogenic carbon loop (–544 t CO_2/a) and district heating displacement of natural gas boilers (–4,831 t CO_2/a), yielding a net balance of 4,034 t CO_2/a. Carbon parity with the Baseline is projected at grid emission factors below 233 g CO_2/kWh.

(4) Seasonal methanol storage is enabled by a modest tank investment (1.1 % of total CAPEX) and achieves 9.1 cycles/a, efficiently buffering the production-demand mismatch driven by the Abwasserverordnung seasonal provisions.

(5) The exergy analysis reveals that waste heat valorization via district heating recovers approximately 1460 MWh_{ex}/a from the electrolyser and substantially more from the CHP fleet, providing the thermodynamic justification for the dominant revenue stream.

Future work should extend the framework to include dynamic grid emission factors, multi-year investment planning under technology cost learning curves, and the integration of additional renewable generation assets (wind, expanded PV) to further reduce grid dependence and increase the share of green hydrogen. Furthermore, more extreme price variations in fossil fuels due to scenarios with supply shortages might be taken into account.

Nomenclature

Symbols

AF	Annuity factor [–]
a	Activity [–]
c	Unit cost [EUR/kWh or EUR/kg]
E	Energy flow [kWh]
F	Faraday constant (96,485 C/mol)
I	Electrical current [A]
M	Molar mass [kg/mol]
$\dot{m}$	Mass flow rate [kg/s]
n	Economic lifetime [a] or number of cells [–]
P	Electrical power [kW]
p	Partial pressure [bar]
Q	Thermal energy [kWh]
R	Universal gas constant (8.314 J/(mol·K))
r	Revenue rate [EUR/kWh or EUR/kg]
T	Temperature [K or °C]
V	Voltage [V]

Greek Symbols

η_act	Activation overpotential [V]
η_conc	Concentration overpotential [V]
η_ohm	Ohmic overpotential [V]
η_el→H2	Electricity-to-hydrogen efficiency [–]

Subscripts and Superscripts

0	Reference state (dead state)
amb	Ambient
cell	Electrolyser cell
el	Electrical
ex	Exergy
i	Asset index
j	Commodity input index
k	Revenue/product output index
source	Heat source
t	Time step index
th	Thermal

Abbreviations

AbwV	Abwasserverordnung (German wastewater ordinance)
BHKW	Combined heat and power unit (Blockheizkraftwerk)
CAPEX	Capital expenditure
CHP	Combined heat and power
DH	District heating
FLH	Full-load hours
LHV	Lower heating value
MeOH	Methanol (CH_3OH)
MILP	Mixed-integer linear programming
mm.esd	Multi-modal energy system design
NG	Natural gas
OPEX	Operational expenditure
PCC	Point of common coupling
PEM	Proton exchange membrane
PPA	Power purchase agreement
PtX	Power-to-X
PV	Photovoltaic
SEC	Specific energy consumption [kWh/kg or kWh/t]
SoC	State of charge [%]

TOTEX Total annualized expenditure [EUR/a]
WACC Weighted average cost of capital
WWTP Wastewater treatment plant

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