Supplementary Digital Material:

Techno-Economic Assessment of Decarbonization Pathways for Methanol and Formaldehyde Production: A Superstructure Optimization Approach

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S1. List of abbreviations

Table S1: List of abbreviations.

Abbreviation	Meaning
ASU	Air Separation Unit
CAPEX	Capital Expenditure
CC	CO_2 Capture
CCS	CO_2 Capture and Storage
CH_2O	Formaldehyde
ETS	Emissions Trading System
IS	Industrial Symbiosis
KPI	Key Performance Indicator
MEA	Monoethanolamine
MeOH	Methanol
MILP	Mixed-Integer Linear Programming
MSW	Municipal Solid Waste
NG	Natural Gas
OPEX	Operational Expenditure
RDF	Refuse-Derived Fuel
STC	Specific Total Cost
T&S	Transport and Storage

Table S2: Configurations for emission mitigation during formaldehyde production.

Abbreviation	Configuration details
NG	Steam methane reforming (SMR)
NG-CC	SMR + MEA-based CC
BG	Biogas tri-reforming
BG-CC	Biogas tri-reforming + MEA-based CC
BM	Biomass gasification
BM-CC	Biomass gasification + MEA-based CC
MSW	MSW gasification
MSW-CC	MSW gasification + MEA-based CC
P2X	Power-to-methanol (direct route)
P2X-CC	Power-to-methanol + MEA-based CC

S2. Process description and data for model development

Formaldehyde production through metal oxide process:

Table S3: Input parameters for the metal oxide process model.

Parameter	Value	Units	Source
Mass & energy balances			
Methanol	1.143	t/t CH_2O	From [1]
Electricity	135	kWh/t CH_2O	From [1]
Saturated steam (12 barg)	2	t/t CH_2O	From [1] and [2]
CO_2	0.018	t/t CH_2O	Average from [1]
DME	0.012	t/t CH_2O	Average from [1]
Economics			
Total CAPEX	9,600,000	USD_{2012}	For 20,000 t CH_2O/y [3]
Lifetime	30	Years	
Discount rate	6%	-	

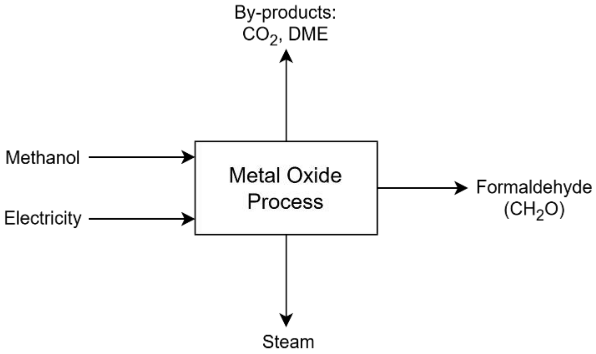

Figure S1: Metal oxide process represented as a black box.

Methanol production routes:

MeOH required for formaldehyde production can be supplied via five different routes.

1) **Steam Methane Reforming (SMR)**: Steam methane reforming, operated at high temperature (700–1100°C, achieved by natural gas combustion) and pressure (20–30 bar), uses natural gas as feedstock and yields syngas, i.e., a mixture of mainly CO, CO_2, and H_2, via reactions (1) and (2) in presence of steam. Subsequent methanol synthesis occurs at moderate temperature (200–300°C) and high pressure (50–100 bar) in a catalytic reactor, according to reactions (3) and (4). The water-methanol mixture obtained is finally separated via distillation, requiring steam.

$$CH_4 + H_2O \rightarrow CO + 3\,H_2 \tag{1}$$
$$CO + H_2O \rightarrow CO_2 + H_2 \tag{2}$$
$$CO + 2\,H_2 \rightarrow CH_3OH \tag{3}$$
$$CO_2 + 3\,H_2 \rightarrow CH_3OH + H_2O \tag{4}$$

2) **Biomass gasification**: Solid biomass (e.g., agricultural or forestry residues, such as wood or straw) is dried and fed to a pressurized steam/oxygen-blown thermal gasifier (~850°C). Oxygen injection partially oxidizes the biomass feed, generating heat for drying, pyrolysis, and gasification reactions. Biomass is converted into bio-syngas, which requires gas cleaning and conditioning to (1) remove tars, ashes, and other impurities, and (2) adjust the H_2/CO ratio via water-gas shift (see reaction (2)). The clean and conditioned syngas is subsequently converted to methanol.
3) **Biogas tri-reforming**: Syngas for methanol production can also be produced from biogas (a mixture of 50–75 vol% CH_4 and 25–50 vol% CO_2). In the present study, biogas is assumed to undergo tri-reforming, combining
   - Steam reforming: $CH_4 + H_2O \rightarrow CO + 3\ H_2$
   - Dry reforming: $CH_4 + CO_2 \rightarrow 2\ CO + 2\ H_2$
   - Partial oxidation of CH_4 and CO to generate heat: $CH_4 + \frac{1}{2} O_2 \rightarrow CO + 2\ H_2$ and $2\ CO + O_2 \rightarrow 2\ CO_2$. The process takes place at high temperature and pressure (1000°C, 20–50 bar) and requires addition of oxygen. Syngas composition can be adapted by external hydrogen addition.
4) **Power-to-Methanol**: CO_2 (captured from biogenic sources, industrial point sources, or Direct Air Capture) is combined with hydrogen (produced by water electrolysis) to produce methanol via direct route (i.e., without reverse water gas shift reaction): $3\ H_2 + CO_2 \leftrightarrow CH_3OH + H_2O$.
5) **Waste-to-Methanol**: Refuse-derived fuel (a fraction of municipal solid waste—assumed to contain 60% biogenic carbon [4]—with higher heating value, obtained after sorting and pre-treatment) undergoes oxygen-blown gasification at high temperature, with direct melting of the inert fraction. From the gasifier exit the desired syngas and an inert slag. Process temperatures vary between 600–800°C in the gasification zone and 1600°C in the melting zone, and heat is assumed to be supplied by natural gas combustion. The obtained syngas is cleaned and conditioned to reach a suitable C/H ratio through water-gas shift and amine-absorption-based CO_2 capture, before subsequent methanol synthesis and purification.

Regarding technology economics, an interest rate of 6% is considered for SMR, while all alternative feedstock options are set at an interest rate of 8%.

Table S4: Input parameters for the models of the methanol production routes.

Parameter	Value	Units	Source
Steam Methane Reforming			
Natural gas (feedstock + heat)	30.4	GJ/t MeOH	From [5]
Water	0.85	t/t MeOH	From [5]
Electricity	74	kWh/t MeOH	From [5]
CO_2 (from combustion)	0.38	t/t MeOH	Computed based on NG demand for heat

CAPEX	31,200,000	USD	For 182 t MeOH/d, from [6]
Biogas reforming			
Biogas	4.10	kWh/kg MeOH	From [7]
Electricity	0.34	kWh/kg MeOH	From [7]
Hydrogen	0.07	kg/kg MeOH	From [7]
Oxygen	0.43	kg/kg MeOH	From [7]
Steam	0.85	kWh/kg MeOH	67% of steam for MeOH distillation, from [7]
CAPEX	2870	€/kW	From [7]
Power-to-MeOH			
Methanol production			
CO_2	1.4	t/t MeOH	From [7]
H_2	0.19	t/t MeOH	From [7]
Electricity (excluding electrolysis)	0.1	MWh/t MeOH	From [7]
Steam	0.58	MWh/t MeOH	From [7]
CAPEX	1350	€/kW	From [7]
Alkaline electrolysis			
Electricity	52	kWh/kg H_2	From [7]
CAPEX	875	€/kW	From [7]
MSW-to-MeOH			
RDF production			
MSW	1.345	MJ/MJ_{RDF}	From [8]
Electricity	0.0245	MJ/MJ_{RDF}	From [8]
RDF gasification			
RDF	8739	kWh/t MeOH	From [9]
Electricity	1594	kWh/t MeOH	From [9]
Oxygen	1.315	t/t MeOH	From [9]
Steam	1469	kWh/t MeOH	From [9]
Natural gas	1061	kWh/t MeOH	From [9]
Slag	0.445	t/t MeOH	From [9]
Captured CO_2	1.519	t/t MeOH	From [9]
Emitted CO_2	0.08	t/t MeOH	From [9]
CAPEX	189,000,000	€$_{2017}$	From [10]

CO_2 capture unit:

Energy requirements (heating, cooling, electricity) and CAPEX are determined based on correlations developed by Kim et al. [11]. An inlet CO_2 fraction of 4 mol% and flue gas flowrate of 0.81 kmol/s are assumed. Heating is assumed to be provided by an external NG-fired boiler.

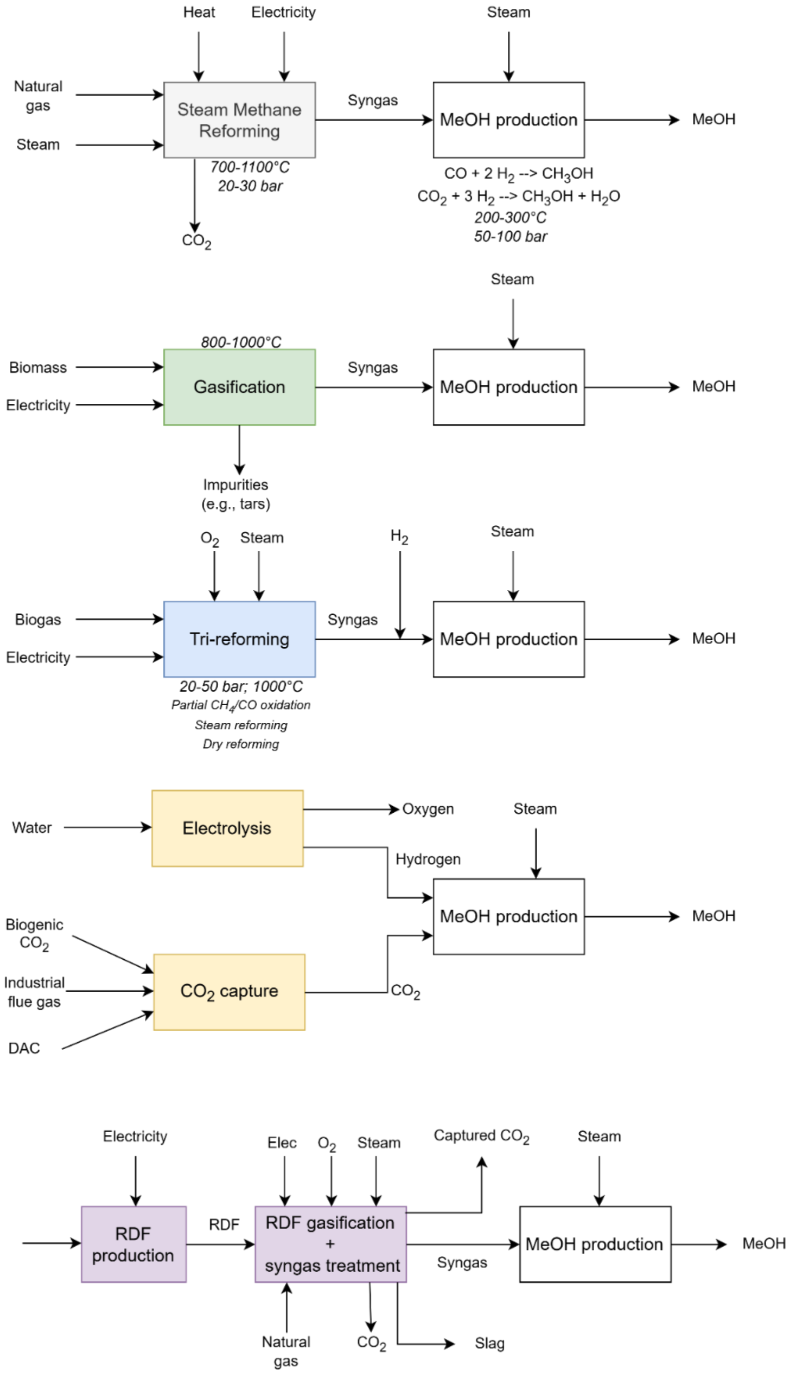

Figure S2: Methanol production routes represented as black boxes.

S3. CO_2 emission factors

Table S5: Indirect emissions for various energy commodities (in kg CO_2/kWh).

Energy commodity	2025	2050	Source
Natural gas	0.039	0.039	[12]
Electricity	0.138	0.057	[13]+ Computed according to eq. (5)
Biogas	0.043	0.043	[14]
Biomass	0.016	0.016	[15]
MSW	0.006	0.006	[4] (transport only)

CO_2 emissions related to electricity production are computed based on (current and future) electricity production mixes [16] and the associated emission factor from the Ecoinvent database [17] [18] [19] [20] [21] [22] [23] [24] [25], according to the equation below.

$$EmF_e = \sum_{t \, \epsilon \, type} s_t \cdot i_t \tag{5}$$

Where s_t and i_t represent, respectively, the share and the specific impact of electricity produced via route t (i.e., wind turbine, solar panels, natural gas, etc.).

Production route t	Share s_t – 2050 scenario	Impact i_t (kgCO_2/kWh)
Wind onshore	32%	0.019
Wind offshore	25%	0.015
Solar	33%	0.090
Other RES	2%	0.063
Hydro and pumped storage	4%	0.315
Nuclear	4%	0.006
Methane	0%	0.501

S4. Total CO_2 emissions for different formaldehyde production routes

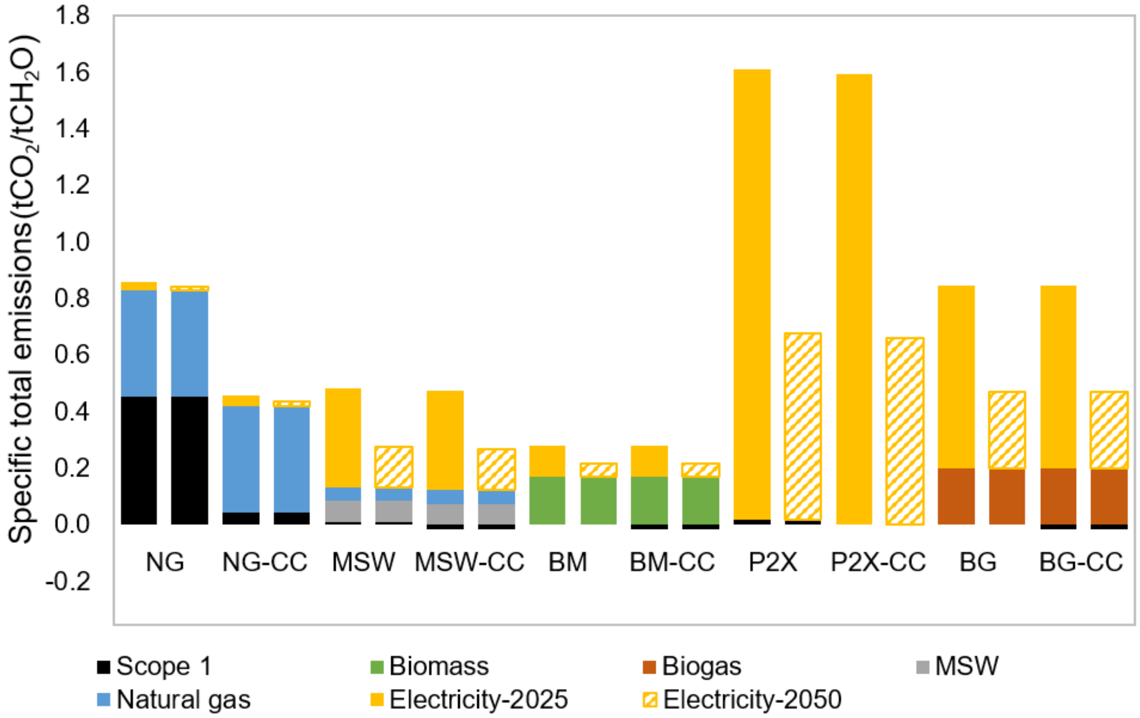

Figure S3: Total CO_2 emissions breakdown by source for different formaldehyde production routes (left bars: electricity is sourced from the current Belgian grid; right bars: electricity is supplied by the 2050 European electricity mix).

S5. Parameter sweep results

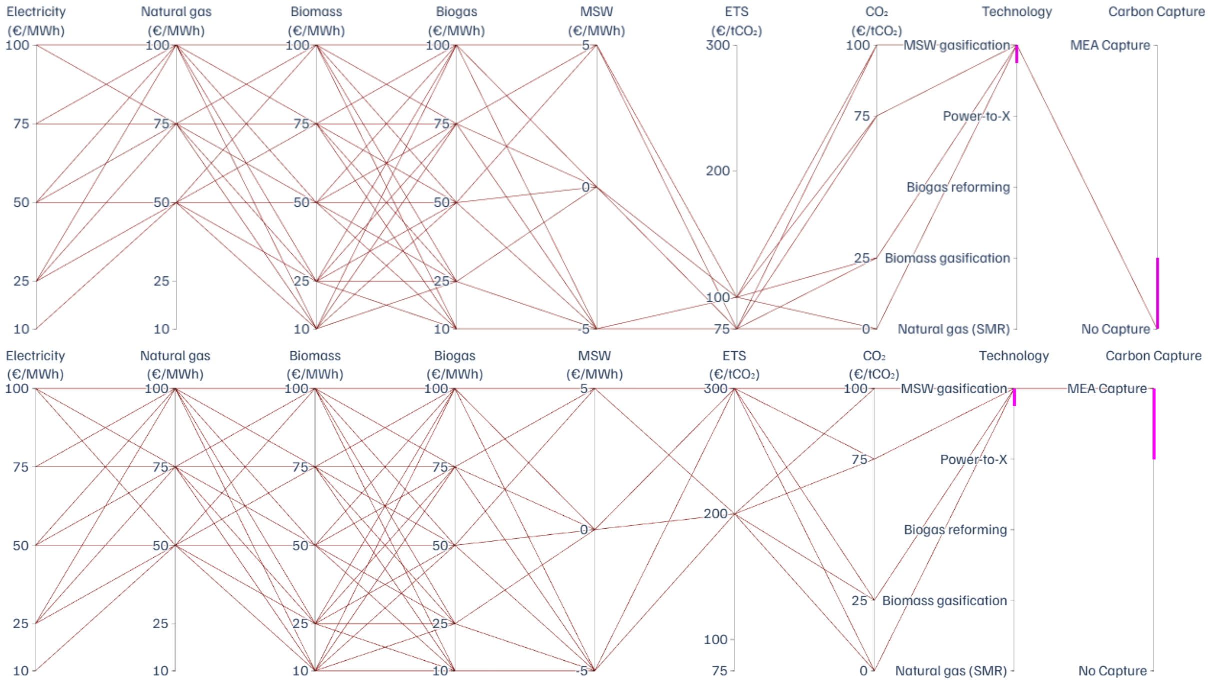

Figure S4: Solution space of economic optimality for MSW (top) and MSW-CC (bottom).

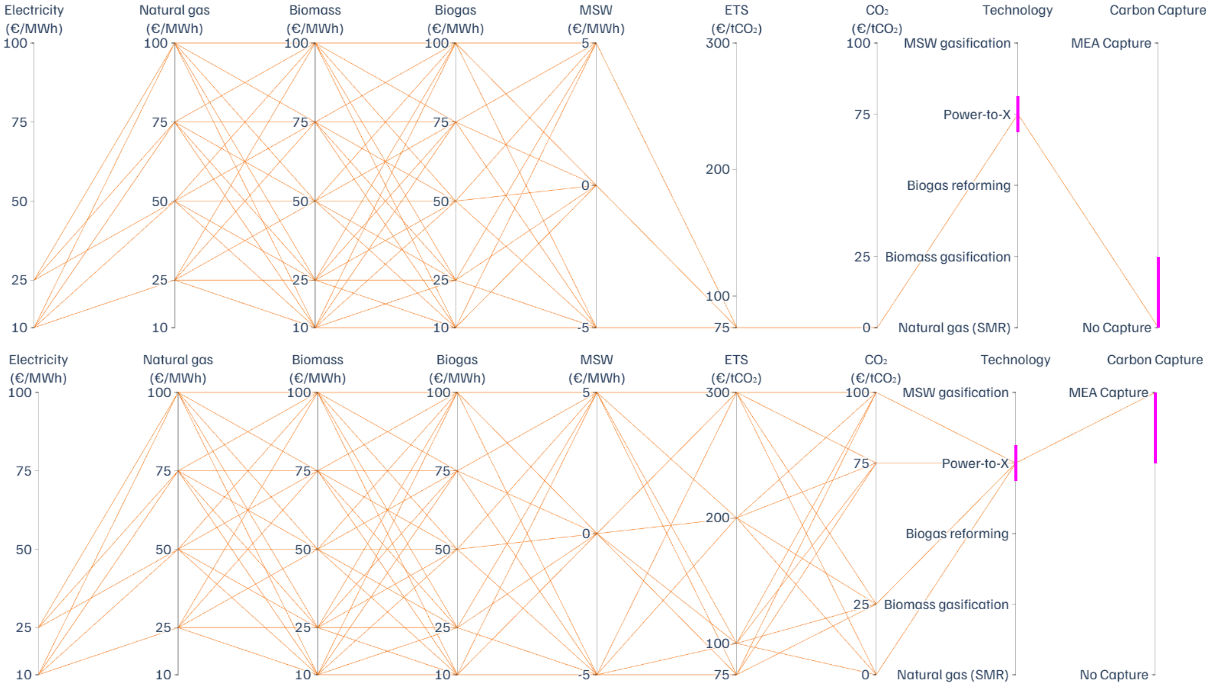

Figure S5: Solution space of economic optimality for P2X (top) and P2X-CC (bottom).

Figure S6: Solution space of economic optimality for BG (top) and BG-CC (bottom).

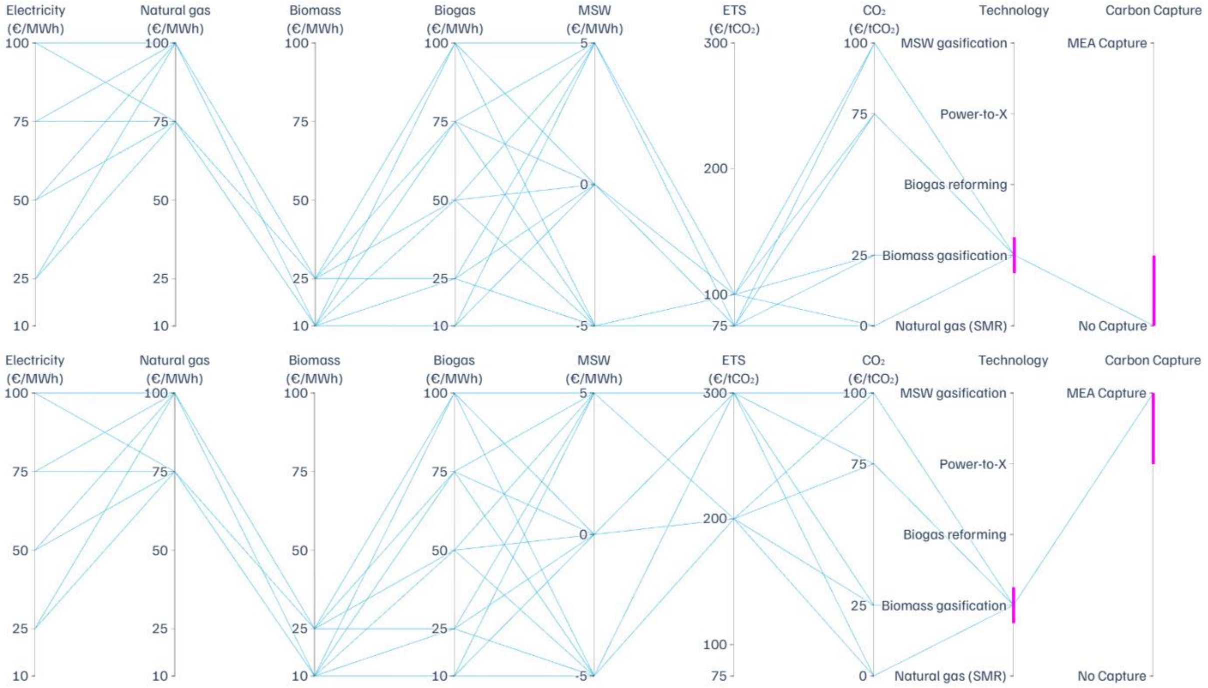

Figure S7: Solution space of economic optimality for BM (top) and BM-CC (bottom).

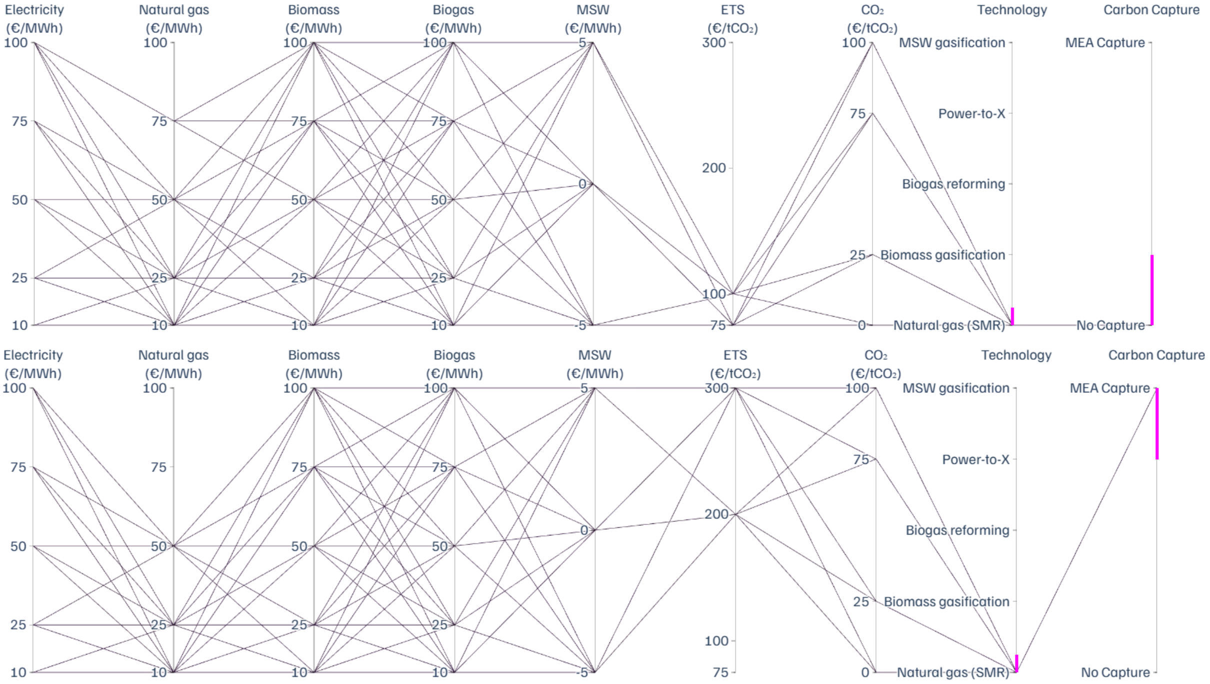

Figure S8: Solution space of economic optimality for NG (top) and NG-CC (bottom).

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