scientific reports

OPEN

Portfolio optimization for industrial cluster defossilization in the Port of Rotterdam

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Defossilizing feedstocks of industrial clusters has increasingly attracted attention due to potential impacts on climate change mitigation targets. However, the transition from fossil-based feedstocks to alternative carbon sources (ACS) presents both environmental and economic challenges in terms of performance and feasibility. One issue is the large uncertainties regarding the techno-economic feasibility in terms of investment decisions, which has been barely studied in the literature at cluster level. This study considers market price fluctuations of raw materials, products and energy over time to evaluate the profit and risk associated with individual plants for decision-making purposes. By adopting Modern Portfolio Theory (MPT), a portfolio optimization problem is defined to provide a risk-return-based guidance framework for transitioning to alternative carbon feedstocks. The proposed optimization model obtains investment portfolios and corresponding production capacity distributions based on the optimal constituents among fossil-based and ACS-based plants. The Port of Rotterdam, the Netherlands, is considered as a case study to assess the defossilization of feedstocks at the cluster level. The results show that integrating ACS-based plants into the cluster requires substantial capital investment, and reduces the Return on Investment (RoI) relative to the associated risk, making full defossilization economically challenging to achieve. However, applying a price-allocation method for re-costing ACS-based (by-)products considering governmental financial supports, the transition to alternative carbon sources can become attractive to investors at specific production capacities, as identified through optimal risk–return portfolios.

Carbon-neutral targets have drawn attention and efforts toward reducing emissions and increasing circularity in recent years[1,2]. As one of the key actions, defossilizing fossil-based chemicals can contribute to sustainable development goals and emission reductions by introducing alternative carbon sources (ACS) to replace fossil-based feedstocks[3–5]. This has triggered research into understanding defossilization from various perspectives, such as identifying alternative pathways and novel technologies, conducting techno-economic and feasibility analyses, performing life cycle assessments, and exploring policy and investment implications. Furthermore, as a proof of concept, location-specific consequences of the defossilization have also been investigated on practical impacts to guide decision-makers in either taking feasible actions or revising policies to ensure reliability and practicality to further generalize them.

Literature review

(i) *How is industrial defossilization understood in the literature?* Due to its importance, defossilization has been explored from various points of view. Several studies have aimed to identify potential ACS and the corresponding technologies and process pathways, and to analyze them from technical, environmental and economical perspectives. For instance, Lopez et al.[6] identified electricity-based and biomass-based methanol as promising and economically competitive transition pathways for defossilization. Zuiderveen et al.[7] evaluated alternative production routes for benzene, toluene, and xylene from an environmental perspective and proposed key factors for emission reduction. Berger et al.[8] conducted a techno-economic feasibility analysis of three production pathways, namely bio-isobutylene production, CO_2 electrolysis for ethanol production, and CO_2 electrolysis for syngas production.

While the aforementioned studies and others highlight the environmental and economic challenges, and potentials of defossilization for stand-alone plants, investigating the impacts of this transition at the cluster level can offer more realistic and practical insights. Chemical and petrochemical clusters are among the largest contributors to CO_2 emissions, as they consist of number of interconnected plants and processing units. These interconnections, through shared materials, utilities, and infrastructures, should also be taken into account,

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since replacing fossil-based technologies with ACS-based plants can significantly affect the entire system due to their differing characteristics. In this regard, a number of studies addressed the transition from fossil-based fuels, focusing on aspects such as modeling the transition[9,10], and assessing environmental and techno-economic implications[11–13].

Such technical studies identify environmental and economic factors in which decision-makers can define policies related to defossilization accordingly[5,14]. These policies are important as they emphasize the need for further technical development, detailed evaluations, and defining the roles of different stakeholders, such as academia, government, and investors, to facilitate the transition from fossil-based fuels towards a more sustainable environment[15]. Despite growing attention to technical feasibility at both process and cluster levels, the transition from fossil-based resources still lacks thorough investigation from an investment and economic perspective, particularly with respect to market price variability and investor-oriented risk-return trade-offs, in contrast to conventional techno-economic analyses. Therefore, developing a framework for such an investigation is essential to guide policymakers, governments, and investors in synthesizing the economic dimensions of defossilization based on an investment strategy[4].

(ii) *How to design investment strategies?* While net present value (NPV)[16] is a conventional metric for profitability analysis and investment planning, it is limited in its ability to capture the systemic interactions and integration effects across multiple plants, particularly at the cluster level. As an alternative, Modern Portfolio Theory (MPT)[17] determines portfolio constituents and their respective investment allocations based on return–risk indicators derived from historical price data, consequently guiding investors toward constructing attractive portfolios. The MPT, as a proven and powerful tool for designing investment strategies, has been applied across various sectors such as energy systems[18], environmental investment planning[19], and chemical production process portfolios[20,21].

Gaining insights into investments related to the transition from fossil-based feedstocks is also a crucial aspect for decision- and policy-makers, given the significant capital requirements, transition uncertainties, and the lack of realistic investment strategies. Therefore, adopting Modern Portfolio Theory (MPT) for this specific problem, i.e. the transition from fossil-based feedstocks to ACS, provides a systematic framework for investment analysis in order to find practical insights to the following: (a) it enables the estimation of the expected Return on Investment (RoI) for different portfolio constituents during the transition based on the risk (i.e. investment viability) involved; (b) it supports the optimal selection of portfolios along with their corresponding individual plant production capacities, highlighting the potential for a gradual transition towards full defossilization if economically feasible; and (c) it identifies the key investment-related obstacles on the required actions of this transition based on a mathematical framework.

(iii) *The Port of Rotterdam as a location-specific investigation:* The Port of Rotterdam (PoR), as a large and interconnected petrochemical cluster and a major contributor to chemical productions in Europe, is as an ideal case study for investigation. It not only offers a reliable benchmark for extending findings to other regions, but also provides practical insights that can inform serious and urgent actions required at the site. Given its significance, the Port of Rotterdam has been the focus of several studies across the aforementioned areas. For instance, Samadi et al.[22] proposed deep decarbonization scenarios, capable of achieving significant reductions in the energy sector of the Port of Rotterdam. Stepchuk et al.[11] investigated the transition from fossil-based fuels in the existing methyl-tert-butyl-ether (MTBE) production at the Port, analyzing both environmental and techno-economic aspects at the process and cluster levels. Similarly, Manalal et al.[12] explored the consequences of replacing fossil-based feedstocks with ACS for ethylene production, emphasizing the need for a major restructuring of mass and energy connections within the cluster. In this regard, Schneider et al.[13] analyzed the broader impact of the transition, including the Port of Rotterdam, using a techno-economic bottom-up model, identifying major challenges in production network management and increased costs. Additionally, Cuppen et al.[9] and Tan et al.[10] developed models of the Port to explore socio-technical boundary objects and levels of system integration, respectively, in support of sustainability transitions. However, a specific exploration of investment strategies for the Port to unraveling viable investment scenarios during the transition is still lacking.

Paper contributions and structure

Placing the above pieces as the identified gaps in the literature and the need for further exploration in the direction of investment, this paper proposes an MPT-based portfolio optimization for the Port of Rotterdam, which incorporates the transition away from fossil-based feedstocks. An extended systematic framework enables the exploration of investment challenges and potentials for the Port of Rotterdam at both the process and cluster levels. Since this approach relies on historical market prices, the required data is collected, and the respective economic parameters, namely RoIs, standard deviations, and correlation factors, are calculated accordingly. Besides investigating portfolio constituents based on market-based economic parameters, a modified allocation method is employed to re-cost the prices of (by-)products from ACS-based plants to make them more attractive and profitable for investors. An additional set of portfolio constituents is also explored to support decision- and policy-makers in developing investment strategies. These analyses not only reveal the challenges and potentials of the transition towards ACS in the Port of Rotterdam using a systematic optimization model, but also highlight hidden angles for governmental financial supports and stakeholder policy adjustments.

The paper is organized as follows. "Problem statement" section includes the problem definition and the developed optimization model based on the MPT for the transition towards ACS. "Description of the Port of Rotterdam" section specifies the specifications of the Port of Rotterdam, including data collection, calculation of economic parameters and metrics, and re-costing parameters with the corresponding calculations. Transition scenarios for some value chains are also defined in this section for subsequent analyses. In "Results and discussions" section, the proposed optimization model is applied to the defined scenarios to explore investment strategies for the Port of Rotterdam. This section presents detailed technical discussions and key observations for each scenario, along with a holistic overview of the transition from an investment perspective. Conclusions are drawn in the final section.

Problem statement

To identify an optimal selection and production distribution among various potential chemical plants within a cluster, an optimization problem can be defined. In this paper, the optimal solution is determined based on profitability and profit volatility according to price fluctuations. This approach aligns with the principles of Modern Portfolio Theory (MPT)[23]. Accordingly, this section introduces an optimization problem that addresses the transition of industrial clusters from fossil-based resources by taking investment perspectives into account. An MPT-based optimization model is, therefore, formulated, and a detailed problem formulation is presented in this section along with the underlying assumptions associated with the transition from fossil-based feedstocks.

Each cluster consists of a number of interconnected plants aligned with several value chains. To defossilize feedstocks, some of these plants should be either replaced or interconnected with ACS-based plants to incorporate ACS. This transition can be defined from various perspectives according to environmental and economic metrics. This paper defines such a transition with respect to investment interests and motives. Therefore, The aim is to determine financial investment shares and corresponding production distributions when incorporating ACS-based technologies into the cluster and reducing the productions of fossil-based plants. This techno-economic assessment requires historical market price variations to calculate the return and risk of investment for each individual plant. This information is used to identify the Pareto front by selecting among existing and potential technologies to maximize RoI while minimizing the risk per investment.

According to the above problem definition, a bi-objective optimization problem can be introduced as follows:

- *Inputs*: RoI and risk of each stand-alone plant, and correlation factors among different plants;
- *Objectives*: Maximize RoI and minimize risk of a potential portfolio;
- *Decision variables*: Investment allocation and corresponding plants' productions for the optimal portfolio constituents;
- *Constraints*: A bound on the total investment, and bounds on plants' productions;
- *Outputs*: A Pareto front for various investment allocations and plants' productions for a potential portfolio.

This problem falls within an MPT-based optimization framework[20,23] that addresses risk-return relationships. In the following section, the mathematical formulation of the MPT-based optimization and its adaptation to the defined problem i.e., the transition from fossil-based feedstocks, are presented.

Optimization model

MPT optimization

Modern Portfolio Theory introduces an analytical optimization framework to optimize the risk-return relationship of a portfolio[23]. In principal, the goal is to find an optimal allocation among $N \geq 2$ assets such that maximizes the return and minimizes the risk for a portfolio. In this regard, the return of a portfolio, $\mu_{\text{portfolio}}$, is then determined as

$$\mu_{\text{portfolio}} = \mathrm{W}^T \boldsymbol{\mu} \tag{1}$$

in which $\mathrm{W} \in \mathbb{R}^N_{\geq 0, \leq 1}$ is the vector of fraction weights of N number of assets in the portfolio, i.e. $\mathrm{W} = [w_1, w_2, ..., w_N]^T$, and $\boldsymbol{\mu} \in \mathbb{R}^N$ encompasses the average of the return of each individual asset in the portfolio over a studied period, i.e. $\boldsymbol{\mu} = [\mu_1, \mu_2, ..., \mu_N]^T$. Furthermore, the risk of the portfolio, $\sigma_{\text{portfolio}}$, is the standard deviation of the portfolio RoIs as follows:

$$\sigma^2_{\text{portfolio}} = \mathrm{W}^T \boldsymbol{\Sigma} \boldsymbol{\Phi} \boldsymbol{\Sigma} \mathrm{W} \tag{2}$$

in which $\boldsymbol{\Phi} \in \mathbb{R}^{N \times N}$ is the symmetric correlation matrix and $\boldsymbol{\Sigma} = \mathrm{diag}(\sigma_1, \sigma_2, ..., \sigma_N) \in \mathbb{R}^{N \times N}$ is the diagonal matrix containing the standard deviation of individual assets over the specific period of time in the portfolio. Therefore, the bi-objective MPT optimization problem to find the optimal fraction weights in order to maximizing the portfolio return, and minimizing the portfolio standard deviation can be written as follows:

$$\begin{cases} \max\limits_{\mathrm{W}} & \mu_{\text{portfolio}} \\ \min\limits_{\mathrm{W}} & \sigma_{\text{portfolio}} \end{cases} \tag{3a}$$

$$\text{s.t.} \quad \mathrm{W}^T \mathbf{1} = 1 \tag{3b}$$

where $\mathbf{1} = [1, 1, ..., 1]^T \in \mathbb{N}^N$.

MPT-based optimization for industrial clusters

Taking the conventional MPT optimization problem into account, a similar MPT-based formulation can be defined for the problem described in "Problem statement" section. Inspired by the work of Shehab et al.[20,21], plants are treated as assets, and the average RoI of each stand-alone plant over a time period is considered equivalent to the average return of each asset in the MPT framework. Therefore, the capital expenditure of an individual plant, as the investment required to acquire a technology, is the same to the capital cost of an asset in the MPT framework. The flowchart of the proposed methodology based on the concept of the modern portfolio theory is summarized in Figure 1, where the details of the mathematical equations are given in the this section. Assuming the linear plant capital cost model[11,20], the allocated investment weight of plant p in a portfolio consisting of N plants denoted by w_p can be defined as follows:

$$w_p = \frac{c_p\ T_p}{\sum_{n=1}^{N} c_n\ T_n} \tag{4}$$

where T_p expresses the total capital cost of the plant p, and c_p denotes its corresponding scaling factor, which relates to plant's production. While the linear cost-scaling model provides reasonable insights, costs in practical applications often change exponentially with the scaling factor at higher capacity[24]. Therefore, inclusion of exponent scaling factor is also discussed in Section S.5 in supplementary materials B.

By defining (4), the constraint (3b) can be satisfied for different portfolios in terms of investment allocation across plants, and two other constraints regarding a bound on total investment, and upper and lower scaling factor (production) limits on individual plants can be then included. The decision variables are then these scaling factors by optimizing the risk-return relationship. By finding the scaling factors, the corresponding investment weights can also be found using (4). Hence, the MPT-based optimization problem (3) can be rewritten for a portfolio of an industrial cluster as follows:

$$\begin{cases} \max\limits_{\mathrm{C}} & \mu_{\text{portfolio}} \\ \min\limits_{\mathrm{C}} & \sigma_{\text{portfolio}} \end{cases} \tag{5a}$$

$$\text{s.t.} \quad c_n^{ll} \le c_n \le c_n^{ul};\ 1 \le n \le N \tag{5b}$$

$$\sum_{n=1}^{N} c_n\ T_n \le I_{tot} \tag{5c}$$

where $\mathrm{C} = [c_1, c_2, ..., c_N]^T \in \mathbb{R}^N_{\ge 0}$ is the vector of scaling factors for the plants in a portfolio. c_n^{ll}, c_n^{ul}, and I_{tot} denote the lower and upper limits on a scaling factors and the total investment in the portfolio, respectively. It should be noted that, since each plant involves different products, the scaling factor is defined based on a reference product of the plant, and productions of other products of a plant can be then calculated according to stoichiometric equivalents.

As mentioned in "Problem statement" section, the problem investigated in this paper concerns the assessment of investment distribution and its shift resulting from the transition from fossil-based feedstocks to ACS for an existing cluster. To be able to accurately mimic the current material steam flows for either external sales, or internal exchanges, the boundaries of constraints (5b) and (5c) should be then adjusted based on the case study and the chosen transition pathway. Additionally, to avoid expanding fossil-based production, which contradicts the transition goal, and fulfill the current demands (instead of reduction in demands) during transition to capital-intensive ACS-based plants, an additional production-related equality constraint is incorporated into the optimization model (5) as follows:

$$\sum_{n=1}^{N} c_n\ m_{n,r}\ P_n = D_r \tag{6}$$

where $m_{n,r}$ expresses the mass stoichiometry of resource or product r for plant n. In other words, this parameter is defined as resource or product per ton of a reference product produced per ton, which means $m_{n,r} = 1$ for the reference product of the plant. Furthermore, P_n denotes the maximum production with respect to the reference product of plant n assigned by the initial design, and D_r is the required demand for product r. This definition

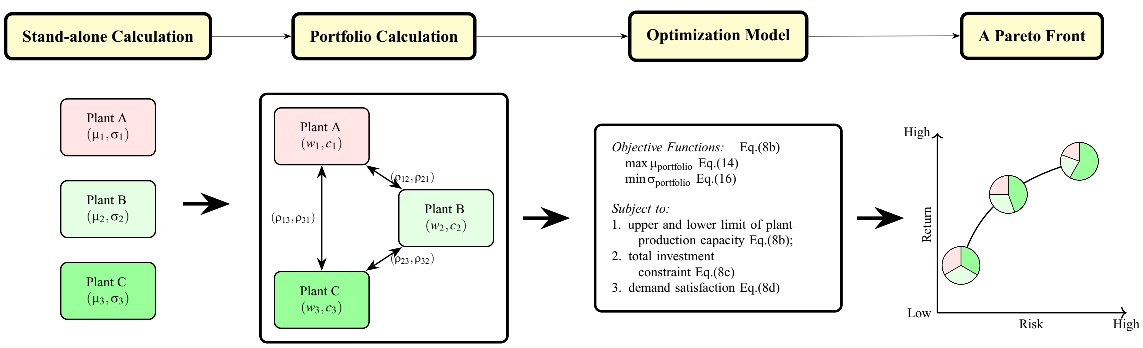


Fig. 1. Schematic overview for the MPT-based methodology: From stand-alone plant analysis to Pareto front results.

ensures modeling an existing cluster with consideration of exact internal exchanges and external sales. If one is interested in extra sales, this equality constraint can be replaced with inequality constraint as follows:

$$\sum_{n=1}^{N} c_n \; m_{n,r} \; P_n \geq D_r \tag{7}$$

Moreover, to assess how hard is primary equality constraint is, a validation via slack variables with penalties is conducted in Section S.6 in supplementary materials B.

According to (5), the portfolio selection results from a bi-objective optimization. Different solution methods can be used for solving the optimization problem such as weighted-sum and $\epsilon-$constraint methods. According to the solution method discussed in the reference MPT book[23], a single objective function that trades off both risk and return can be defined as follows:

$$\max_{\mathrm{C}} \quad \lambda \mu_{\mathrm{portfolio}} - (1-\lambda)\sigma_{\mathrm{portfolio}} \tag{8}$$

in which $\lambda \in [0, 1]$ is the weighted factor to trade off between the return and risk, where in practice is set by an investor according to their interest of a trade-off between risk and return. By changing λ between zero and one, a Pareto front can be obtained. Therefore, the complete optimization model can be written as follows:

$$\max_{\mathrm{C}} \quad \lambda \mu_{\mathrm{portfolio}} - (1-\lambda)\sigma_{\mathrm{portfolio}} \tag{9a}$$

$$\text{s.t.} \quad c_n^{ll} \leq c_n \leq c_n^{ul}, \quad 1 \leq n \leq N \tag{9b}$$

$$\sum_{n=1}^{N} c_n \, T_n \leq I_{tot} \tag{9c}$$

$$\sum_{n=1}^{N} c_n \, m_{n,r} \, P_n = D_r \tag{9d}$$

Although, to follow the origin of modern portfolio theory, the weighted-sum method is considered as a primary solution method, to complementing assessment, the $\epsilon-$constrain method by fixing one objective, while optimizing the other is also considered as a secondary solution method. In this scenario, portfolio return is maximized subject to a constraint on the portfolio risk. Therefore, the optimization problem presented in (9a)-(9d) can be rewritten as follows:

$$\max_{\mathrm{C}} \quad \mu_{\mathrm{portfolio}} \tag{10a}$$

$$\text{s.t.} \quad \sigma_{\mathrm{portfolio}} \leq \epsilon \tag{10b}$$

$$c_n^{ll} \leq c_n \leq c_n^{ul}, \quad 1 \leq n \leq N \tag{10c}$$

$$\sum_{n=1}^{N} c_n \, T_n \leq I_{tot} \tag{10d}$$

$$\sum_{n=1}^{N} c_n \, m_{n,r} \, P_n = D_r \tag{10e}$$

in which ϵ varies between the maximum and minimum possible risks, which yields in a Pareto front. In summary, the proposed optimization model provides a systematic framework for assessing the transition from fossil-based feedstocks to ACS. The effects of constraint boundaries, total investment, and the production rate of a specific value chain are investigated in the following sections based on primary solution method, while an assessment of the $\epsilon-$constraint method is also conducted to investigated distributed solutions. The next section presents the details of the parameters and data required to run the optimization model for the Port of Rotterdam.

Description of the Port of Rotterdam

The Port of Rotterdam is an interconnected industrial cluster comprising multiple companies that share materials and utilities across different value chains. The cluster includes a variety of chemical plants producing numerous chemicals. The level of integration and complexity of the Port of Rotterdam cluster has been modeled and investigated by Tan et al.[10]. Due to the high level of integration, replacing a fossil-based feedstock can significantly affect value chains through changes in material and utility streams.

To apply the proposed optimization model for assessing investment allocation and corresponding scaling factors in the transition to ACS, a part of the Port of Rotterdam is considered. This part includes six fossil-based plants, each forming part of different value chains. A number of key chemicals, namely ethylene, benzene, propylene-glycol-methyl-ether (PGME), MTBE, styrene, propylene oxide, and propylene glycol, are taken into account. Six ACS-based plants are considered to replace fossil-based resources, which are methanol-to-olefins, methanol-to-aromatics, plastic waste pyrolysis, biomass-to-isobutylene via organosolv, CO2-to-methanol via hydrogenation, and CO2-to-ethylene via electrochemical reduction. The details of fossil-based and ACS-based plants such as resources, reference products, and the corresponding production capacities and capital expenditures are given in Table 1. This information comes from bottom-up process models at equipment level, which allows to obtain equipment lists, and material and energy balances of each plant (supplementary materials A).

In addition to resources and (by-)products, utility streams are also accounted for in the plant modeling and revenue calculations, namely electricity, hydrogen, CO2, oxygen, low-low pressure steam (LLPS), low pressure steam (LPS), medium pressure steam (MPS), and high pressure steam (HPS).

The flow of either mass or utility streams can be then determined as follows:

$$\bar{c}_p \; m_{p,r} = f_{p,r} \tag{11}$$

where the definition of the parameter $m_{p,r}$ is the one introduced in "Optimization model" section, i.e. the mass or utility stoichiometry of either resource, product or energy and utility *r* for the plant *p*. In addition, $\bar{c}_p$ expresses the nominal modeled production (based on the bottom-up model) of the reference product (as given in Table 1), and $f_{p,r}$ denotes the net amount of either the mass or utility flow *r* for the plant *p*. In this way, all potential material exchanges among plants with the cluster are embedded into the proposed model, in which no further direct constraints regarding mass and utility is required, unless specific constraints besides what already existed needs to be defined. It should be noted that net flows for inputs (resource consumption and energy demand) are negative, whereas net flows for outputs (product and energy generation) are positive. Based on the net flow amounts of the streams, other economic parameters, such as gross value added, profitability, and RoI can be calculated accordingly, as it is discussed in the following sections. The mass and energy stoichiometric parameters, i.e. $m_{p,r}$ are given in Table 2 for the considered plants.

Collection of histrionical data for prices

The flows of mass and energy define the respective requirements and outputs for each plant. Accordingly, by using the prices of materials and utilities, the gross value added of plant *p*, denoted by G_p, can be calculated as follows:

$$G_p = \sum_r \varrho_r \; f_{p,r} \tag{12}$$

	Plant	Reference product	Production[1]($\bar{c}_p$ [kt/month])	Capital expenditures (T_p [M€])	By-product(s)	Resource(s)
Fossil-based plants						
1	Ethylbenzene production	Ethylbenzene	65.32	32.87	-	Benzene Ethylene
2	MTBE production	Methyl tert-butyl ether	33.21	30.67	Isobutylene	Methanol Tert butyl alcohol
3	Olefins	Ethylene	73.18	1031.93	Benzene Propylene	Naphtha H2
4	Propylene oxide/tert-butyl alcohol production	Propylene oxide	21.13	193.01	Tert-butyl alcohol	Propylene Butane, O2
5	Propylene glycol production	Propylene glycol methyl ether	7.47	20.12	–	Methanol Propylene oxide
6	Propylene oxide/Styrene monomer production	Propylene oxide	24.63	284.07	Styrene	Ethylbenzene Propylene
	ACS-based plants					
7	Methanol-to-olefins	Ethylene	26.2	322.04	Benzene, Propylene	Methanol
8	Methanol-to-aromatics	Benzene	44.36	2796.31	Ethylene, Propylene Butane, P-xylene	Methanol, H2
9	plastic waste pyrolysis	Naphtha	87.5	788.16	Diesel, Vacuum gas oil Benzene	Polypropylene Polyethylene, H2
10	Biomass-to-isobutylene via organosolv	Isobutylene	29.87	2004	–	Biomass
11	CO2-to-methanol via hydrogeneration	Methanol	33.61	431.45	–	CO2, H2
12	Electrochemical reduction of CO2-to-ethylene	Ethylene	27.35	646.92	–	CO2

Table 1. Plant configurations considered for industrial cluster portfolio analysis of the Port of Rotterdam. [1]The values for the nominal productions are taken from the model proposed by Tan et al[10].

Plant → Material/Utility[1,2] ↓	Fossil-based plants						ACS-based plants					
	Ethylbenzene production	MTBE production	Olefins	Propylene oxide production	Propylene glycol production	Styrene monomer production	Methanol-to-olefins	Methanol-to-aromatics	Waste plastic pyrolysis	Biomass-to-isobutylene via organosolv	CO2-to-methanol via hydrogeneration	Electrochemical reduction of CO2-to-ethylene
Ethylene oxide	–	–	–	–	–	–	–	–	–	–	–	–
Ethylene	-0.26798	–	1.00000	–	–	–	1.00000	0.03861	–	–	–	1.00000
Ethylbenzene	1.00000	–	–	–	–	-2.65177	–	–	–	–	–	–
Benzene	-0.74826	–	0.77993	–	–	–	0.25362	1.00000	0.00420	–	–	–
Methanol	–	-0.38000	–	–	-0.40173	–	-7.31732	-16.53196	–	–	1.00000	–
MTBE	–	1.00000	–	–	–	–	–	–	–	–	–	–
Tert butyl alcohol	–	-1.25750	–	2.30789	–	–	–	–	–	–	–	–
Isobutane	–	–	– 3.41606	–	–	–	–	–	–	–	–	–
Naphtha	–	–	0.56643	-	–	–	–	–	1.00000	-	–	–
Propylene	–	–	–	-0.74318	–	-0.84896	1.26493	0.12731	–	–	–	–
Butane	–	–	–	-2.15824	-	-	-	1.55805	–	–	–	–
Propylene oxide	–	–	–	1.00000	-0.79679	1.00000	-	–	–	–	–	–
PGME	–	–	–	-	1.00000	-	-	–	–	–	–	–
Styrene	–	–	–	-	-	2.25449	-	–	–	–	–	–
O-xylene	–	–	–	–	–	–	–	0.00907	–	–	–	–
P-xylene	–	–	–	–	–	–	–	1.82582	–	–	–	–
Diesel	–	–	–	–	–	–	–	–	1.38708	–	–	–
Vacuum gas oil	–	–	–	–	–	–	–	–	1.26970	–	–	–
Isobutylene	–	0.24250	–	–	–	–	–	–	–	1.00000	–	–
Polypropylene	–	–	–	–	–	–	–	–	-2.33338	–	–	–
Polyethylene	–	–	–	–	–	–	–	–	-2.38100	–	–	–
Biomass	–	–	–	–	–	–	–	–	–	-2.90994	–	–
CO2	–	–	–	–	–	–	–	–	–	–	-1.98374	-4.60022
O2	–	–	–	-1.03107	–	–	–	–	–	–	–	5.58698
H2	–	–	–0.00133	–	–	-0.01217	–	-0.03246	-0.01536	–	-0.027276	–
LLPS	1.24086	0.78250	–	-23.07980	-0.44470	-10.49823	–	–	–	-8.08701	1.88858	-0.97581
LPS	0.38878	-0.09500	– 5.92988	-5.39475	–	-2.27701	-20.67963	22.58158	4.63983	–	4.69890	1.77642
MPS	-0.08449	-1.54500	4.08823	-2.58761	-6.14103	-25.19211	3.51221	-8.43788	2.83657	-18.68382	0.66650	3.75182
HPS	-1.50830	–	8.75022	–	-0.05503	–	0.21690	0.02893	29.49219	–	–	–
Electricity	-0.01099	-0.10500	– 1.54629	-0.60832	-0.01398	-0.91655	-0.24013	-0.56288	-0.00797	-35.69446	-4.35690	-12.20588

Table 2. Stoichiometric parameter of mass or energy *r* for plant *p* ($m_{p,r}$). [1]The units of the stoichiometric parameters with respect to mass and energy are $\frac{kt_{\text{mass r}}}{kt_{\text{reference product}}}$ and $\frac{GJ_{\text{energy r}}}{kt_{\text{reference product}}}$, respectively. [2]Negative values indicate resource consumption, while positive values indicate product production

where ϱ_r denotes the price of either material or energy r in a specific currency per unit of material or energy. In case the quality of feedstocks varies, its effect should be reflected in this variable, i.e., the price. However, any technical effects of this variation should be modeled upfront with new stoichiometric parameters, which is not within the scope of this study. Since the net flows for inputs are negative and for outputs are positive, the gross value added given by (12) represents the difference between selling outputs and purchasing inputs for each plant. Therefore, prices for materials and energy are required. Moreover, the proposed MPT-based optimization is applied over a defined time period to have an indication of uncertainty, and price data should be then collected over a corresponding time range to enable the calculation of the average, variance, and standard deviation of the gross value added, and subsequently, the average RoI during the studied period.

Historical material prices were collected on a monthly basis for the years 2018–2024. Most of these prices are based on data reported by *businessanalytiq*[25]. A few of material prices is considered fixed based on the recent market price as no histrionical price variation is available (supplementary materials A). Steam prices are derived using the natural gas price, the assumed boiler efficiency, and the cost estimation formula[26]. Once the price of high-pressure steam is calculated, the prices of lower-pressure steams can be derived based on the enthalpy differences between high- and low-pressure steam levels[26]. These calculated prices are also provided in supplementary materials A.

Economic parameters and metrics

This section presents the calculation of economic parameters and metrics required for the optimization model, based on the collected historical monthly prices of materials and energy.

Return of investment for a single plant and a portfolio

The RoI of plant *p*, i.e. R_p as one of the key parameters, can be calculated as follows:

$$R_p = \frac{L_p}{T_p} \times 100 \tag{13}$$

where L_p expresses the gross profit of plant *p*, and T_p denotes the total capital cost of the plant *p* as mentioned before. The total capital costs for each plant (as given in Table 1) are derived from the bare equipment cost[10], along with a breakdown that includes inside battery limits (ISBL), outside battery limits (OSBL), and engineering and contingency costs[16]. The detailed data and breakdown calculations are provided in supplementary materials A. Furthermore, the gross profit can be derived based on the gross value added, fixed cost and depreciation of plant *p* as follows:

$$L_p = G_p - H_p - D_p \tag{14}$$

where H_p and D_p express fixed cost and depreciation of plant *p*, respectively. In this paper, the fixed costs of plant *p* are calculated based on the fixed OPEX breakdown[16], which includes costs related to shift operations, supervision, direct overhead, maintenance, plant overhead, and taxes and insurance. Depreciation is also calculated using the straight-line method, assuming a 20-year plant lifetime and the corresponding capital expenditure. Although depreciation may not be immediately reflected in cash flows, it influences the realistic estimation of profitability and long-term return on an investment[24]. To provide insights into the contributions of both the cost breakdown and depreciation for the Port of Rotterdam, a guideline for investors is provided in Section S.4 in supplementary materials B, based on the real data. It should be also noted that the main contributor to the return is the gross value added of materials and utilities, and other factors primarily serve to complete the calculation. All assumptions, detailed breakdowns, calculations, and resulting data for fixed costs and depreciation are provided in supplementary materials A. Since prices fluctuate over the studied time period (collected on a monthly basis), the average RoI of plant *p*, denoted as $\bar{R}_p$, can be calculated as the average of *j* individual RoI values over that period as follows:

$$\bar{R}_p = \frac{\sum_j R_p}{j} \times 100 \tag{15}$$

The average RoI of a portfolio consisted of *N* plants, i.e. $\bar{R}_{\text{portfolio}}$ (also $\mu_{\text{portfolio}}$ in (9a)), can be written according to (1) as follows:

$$\bar{R}_{\text{portfolio}} = \sum_{n=1}^{N} w_n \, \bar{R}_n \tag{16}$$

Based on the aforementioned data and formulations, the average RoIs for the studied time period are given in Table 3. As can be seen, most of the ACS-based plants demonstrate negative RoI values, due to the expensive technologies they employ. This is also in line with the detailed investigations conducted by Stepchuk et al.[11] and Manalal et al.[12] for MTBE and ethylene production, respectively. However, while the proposed portfolio optimization is applied to these RoI values, the next section discusses the essence of price corrections for the products of ACS-based plants, considering governmental financial support, to highlight how this transition can be made more attractive for investors. Furthermore, negative RoI values for a few fossil-based plants are also considered reasonable due to high fluctuations in prices during the Covid period, as well as announcements regarding the closure of some plants in the Port of Rotterdam, since they are no longer profitable. Internal

Plant	Average RoI ($\bar{R}_p$)	Standard deviation (σ_p)
Fossil-based plants		
Ethylbenzene production	− 3.64	3.99
MTBE production	− 1.57	26.94
Olefins	4.84	1.77
Propylene oxide production	4.51	6.12
Propylene glycol production	8.04	15.97
Styrene monomer production	− 1.18	5.59
ACS-based plants		
Methanol-to-olefins	− 2.13	3.68
Methanol-to-aromatics	− 3.34	1.67
Plastic waste pyrolysis	0.03	11.24
Biomass-to-isobutylene via organosolv	1.29	0.91
CO2-to-methanol via hydrogeneration	− 18.65	7.14
Electrochemical reduction of CO2-to-ethylene	− 9.06	1.45

Table 3. Stand-alone plant return (i.e., the average RoI) and risk (i.e., the standard deviation) based on fluctuations in material and energy prices between 2018 and 2024.

material sharing among plants owned by the same company can also result in a positive RoI at the company level. Therefore, the aforementioned assumptions for both fossil-based and ACS-based plants are applied in the next section to construct another set of RoI values for investigating the portfolio optimization.

Standard deviation of a single plant and a portfolio

Another parameter in the optimization model is the standard deviation of RoIs, which, by definition, is the square root of the variance of RoIs. Therefore, the variance and the standard deviation of plant *p*, denoted as v_p and σ_p, respectively, can be calculated based on *j* individual RoI values over the studied period, as follows:

$$v_p = \frac{\sum_j \left(R_p - \bar{R}_p\right)^2}{j-1} \tag{17a}$$

$$\sigma_p^2 = v_p \tag{17b}$$

The standard deviations are then provided in Table 3. The calculation of standard deviation for a portfolio should be derived based on correlation factors. Given (2), the explicit form for a portfolio with *N* number of plants can be written as

$$\sigma_{\text{portfolio}}^2 = \sum_{n=1}^{N} w_n^2 \sigma_n^2 + 2\sum_{n=1}^{N}\sum_{n \neq m}^{N} w_n w_m \rho_{n,m} \sigma_n \sigma_m \tag{18}$$

where $\rho_{n,m}$ denotes the correlation factor between two plants. This correlation factor represents the strength of the relationship between two plants in terms of how their risks influence each other. It can then be calculated based on *j* individual RoI values over the studied period, as follows:

$$\rho_{n,m} = \frac{\sum_j \left(R_n - \bar{R}_n\right) \times \left(R_m - \bar{R}_m\right)}{\sqrt{\sum_j \left(R_n - \bar{R}_n\right)^2} \times \sqrt{\sum_j \left(R_m - \bar{R}_m\right)^2}} \tag{19}$$

In other words, the correlation factor defines the movement of returns and their relative strength between two plants, represented by a value between -1 and 1. If the correlation factor approaches one, i.e., $\rho_{n,m} \rightarrow 1$, it indicates that the two plants have strongly correlated returns moving in the same direction. Conversely, if the correlation factor approaches minus one, i.e., $\rho_{n,m} \rightarrow -1$, it implies that the returns of the two plants move in opposite directions, but still with a strong inverse relationship[21]. The symmetric correlation matrix, Φ, is given in Table 4.

Re-costing ACS-based prices, RoI, and standard deviation

As calculated in "Economic parameters and metrics" section, the ACS-based plants have negative RoI values. This is primarily due to the employment of capital-intensive emerging technologies and the high consumption of non-fossil feedstocks required to meet production demands. Therefore, using the existing market prices for (by-)products makes the RoI negative. Therefore, governmental financial support can play an important role to make the transition attractive for investors to plan. Based on the proposed model, this can be implemented either through the removal of subsidies for fossil-based plants[27] or the allocation of subsidies to ACS-based

	Plant	1	2	3	4	5	6	7	8	9	10	11	12
1	Ethylbenzene production	1.00											
2	MTBE production	− 0.43	1.00										
3	Olefins	0.44	− 0.22	1.00									
4	Propylene oxide production	− 0.35	− 0.24	− 0.24	1.00								
5	Propylene glycol production	0.36	− 0.18	0.68	− 0.07	1.00							
6	Styrene monomer production	− 0.95	0.48	− 0.56	0.30	− 0.47	1.00						
7	Methanol-to-olefins	− 0.27	0.02	− 0.28	0.55	− 0.19	0.27	1.00					
8	Methanol-to-aromatics	− 0.15	− 0.03	− 0.48	0.45	− 0.46	0.18	0.79	1.00				
9	Plastic waste pyrolysis	0.70	− 0.30	0.15	− 0.26	− 0.29	− 0.60	− 0.03	0.31	1.00			
10	Biomass-to-isobutylene via organosolv	− 0.93	0.57	− 0.28	0.21	− 0.35	0.89	0.13	0.01	− 0.09	1.00		
11	CO2-to-methanol via hydrogeneration	− 0.96	0.54	− 0.46	0.40	− 0.38	0.94	0.25	0.14	− 0.15	0.93	1.00	
12	Electrochemical reduction of CO2-to-ethylene	0.58	− 0.82	0.19	0.19	0.21	− 0.65	0.11	0.24	− 0.12	− 0.76	− 0.66	1.00

Table 4. Symmetric correlation matrix Φ consisting of correlation factors $\rho_{n,m}$ between plant returns.

technologies[28]. More specifically, policy discussions may consider the following three mechanisms, each of which affects the model output as detailed below:

- *Price difference compensation:* Providing subsidies to cover the difference between the prices of fossil-based and ACS-based counterpart plants, which effectively increases the revenue stream of the ACS-based options;
- *Investment credits:* Offsetting the high upfront capital costs of ACS-based technologies, which effectively lowers the denominator in RoI calculations;
- *Carbon taxation:* Increasing taxes on fossil-based technologies, which increases their operating expenses and makes the relative economics of ACS-based technologies more competitive.

Among these three options, we have chosen to implement the first mechanism by re-costing the (by-)products of ACS-based plants. It should be noted that the second method (investment credits) can also be indirectly interpreted through the proposed methodology, as the model provides the total investment and its shares among fossil-based and ACS-based plants. This breakdown allows for a concrete plan based on the required total investment and potential government support. Therefore, re-costing of the (by-)products of ACS-based plants is presented in this section to demonstrate the shift from negative to positive RoI values and to investigate the subsequent effects on the optimization model outputs for decision-makers.

Inspired by various cost allocation methods discussed by Deevski[29], to re-cost the (by-)products of the ACS-based plants and identify reasonable selling values, a comparison is made with their corresponding fossil-based plants (i.e., those that the ACS-based plants are expected to replace fossil-based resources). In this approach, the expenses, including required resources, energy consumption, and allocated fixed costs and capital expenditure, are first calculated for each corresponding fossil-based plant. Then, based on the distribution of the (by-) products in mass and their market prices, price allocation proportions are determined. Using these allocation ratios, the total cost is proportionally distributed among the (by-)products, allowing for the calculation of minimum prices required to fully compensate the production expenses. Next, the difference between the market prices and these minimum prices is used to compute the value-added ratios for each (by-)product. These ratios serve as indicators of economic margin and are applied to the ACS-based plant's (by-)products. Accordingly, the minimum prices of ACS-based (by-)products are calculated using the same cost allocation method, and then the previously derived value-added ratios (from the fossil-based counterparts) are added. This yields a set of re-costed prices for the ACS-based (by-)products. This procedure is mathematically summarized in Section S.1 in supplementary materials B.

According to the proposed procedure for re-costing ACS-based prices, new prices can be derived. In this way, the (by-)products of methanol-to-olefins, methanol-to-aromatics, plastic waste pyrolysis, and electrochemical reduction of CO2-to-ethylene are re-costed based on the added value proportions calculated for the olefins plant's (by-)products and CO2-to-methanol via hydrogenation, and biomass-to-isobutylene with the MTBE plant. These re-costed prices are provided in supplementary materials A. The corresponding governmental financial support, i.e. the subsidy required to achieve these re-costed prices for each ACS-based plant at full production, can also be calculated in a similar way. The respective calculations and derived values are presented Section S.2 in supplementary materials B. All the calculations are based on price fluctuations relative to the baseline fossil-based prices. To mitigate the influence of extreme market volatility, the year 2021, which was marked by significant Covid-related disruptions, has been excluded from the analysis. Therefore, the RoI and standard deviation based on these two assumptions are recalculated and presented in Table 5. Table 6 includes the recalculated symmetric matrix of correlation factors among the plants based on the re-costed prices. Now, these revised economic parameters can be incorporated into the optimization model to enable a comparative analysis with the original parameters calculated in the previous section.

Transition scenario definition

To investigate the transition from fossil-based feedstocks to ACS, a number of scenarios based on the Port of Rotterdam is defined in this section. The transition from fossil-based feedstockes to ACS involves the inclusion

Plant	Average RoI ($\bar{R}_p$)	Standard deviation (σ_p)
Fossil-based plants		
Ethylbenzene production	-3.68	4.07
MTBE production	6.36	18.14
Olefins	4.55	1.60
Propylene oxide production	2.56	3.72
Propylene glycol production	3.73	12.40
Styrene monomer production	1.36	1.91
ACS-based plants		
Methanol-to-olefins	5.79	3.62
Methanol-to-aromatics	1.85	2.05
Plastic waste pyrolysis	9.90	9.96
Biomass-to-isobutylene via organosolv	1.67	1.24
CO2-to-methanol via hydrogeneration	2.91	2.63
Electrochemical reduction of CO2-to-ethylene	6.76	2.85

Table 5. Stand-alone plant return (i.e., the average RoI) and risk (i.e., the standard deviation) based on re-costed prices for ACS-based plants between 2018 and 2024 excluding 2021 due to significant Covid-related disruptions.

	Plant	1	2	3	4	5	6	7	8	9	10	11	12
1	Ethylbenzene production	1.00											
2	MTBE production	− 0.63	1.00										
3	Olefins	0.47	− 0.15	1.00									
4	Propylene oxide production	− 0.37	− 0.24	− 0.28	1.00								
5	Propylene glycol production	0.51	− 0.26	0.53	− 0.10	1.00							
6	Styrene monomer production	− 0.02	0.40	0.15	− 0.25	0.16	1.00						
7	Methanol-to-olefins	− 0.41	0.41	0.49	− 0.14	0.03	0.34	1.00					
8	Methanol-to-aromatics	− 0.67	0.57	0.18	− 0.02	− 0.19	0.33	0.94	1.00				
9	Plastic waste pyrolysis	0.44	0.06	0.50	− 0.45	0.03	0.19	0.18	0.02	1.00			
10	Biomass-to-isobutylene via organosolv	− 0.84	0.74	− 0.27	0.15	− 0.41	0.27	0.62	0.82	− 0.20	1.00		
11	CO2-to-methanol via hydrogeneration	− 0.16	0.82	0.04	− 0.25	0.02	0.49	0.44	0.49	− 0.27	0.69	1.00	
12	Electrochemical reduction of CO2-to-ethylene	− 0.35	0.47	0.29	0.14	− 0.14	0.30	0.74	0.74	− 0.37	0.63	0.51	1.00

Table 6. Symmetric correlation matrix Φ consisting of correlation factors $\rho_{n,m}$ between plant returns based on re-costed prices for ACS-based plants.

of ACS-based plants to supply non-fossil-derived feedstocks. It is important to emphasize that this transition significantly reshapes existing value chains[12], and the scenarios are primarily defined around main chemical blocks and the production of key products that serve as building blocks for downstream processes. Hence, the focus should be directed toward investment decisions and production distributions related to actual replacements and integrations for a value chain.

Potential scenarios are defined and presented in Table 7. The Port of Rotterdam can be then evaluated from an investment portfolio perspective for the transition from fossil-based feedstocks, using the proposed optimization model across these various scenarios, which is discussed in the next section. Additionally, the role of integrating plastic waste pyrolysis is also discussed separately in Section S.3 in supplementary materials B, for Scenarios 1 and 2 to evaluate the potential for full defossilization by fully supplying naphtha to the olefins plant, since this transition does not affect downstream processes.

Results and discussions

In this section, the proposed portfolio optimization model for the defined scenarios are applied and risk-return relationships are found for the transition from fossil-based feedstocks in the Port pf Rotterdam. The data and parameters provided in "Description of the Port of Rotterdam" section are used, and additional assumptions and constraints (if applicable) specific to each scenario are mentioned accordingly. Therefore, for the market-based economic parameters, values from Tables 3 and 4 are fed into the optimization model, and for the re-costed parameters, values from Tables 5 and 6 are used. The optimization problems for the various scenarios are modeled in MATLAB solved by a `fmincon` function within a loop to find the Pareto front on a laptop with an Intel Core i7 1.70 GHz processor and 16 GB RAM. The initialization strategy is considered deterministic, i.e. the total investment budget is initially allocated across all candidate plants proportional to their specific capital costs,

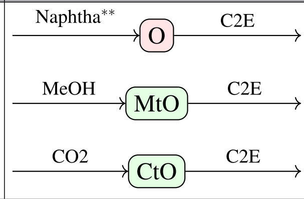
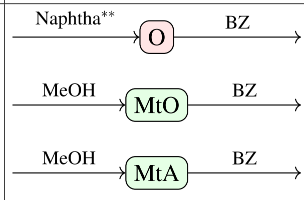
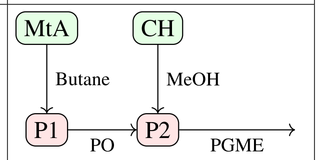
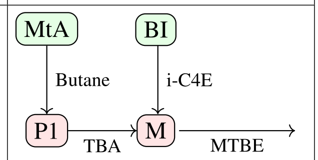
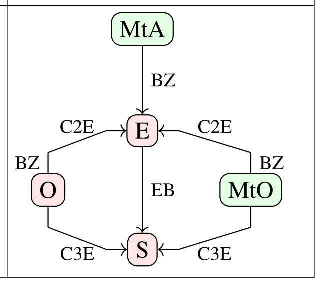
Scenario	Plants	Purpose(s)	Simplified connection*
1	Olefins (O) Methanol-to-olefins (MtO) CO2-to-ethylene (CtO)	To replace the olefins plant for ethylene production	
2	Olefins (O) Methanol-to-olefins (MtO) Methanol-to-aromatics (MtA)	To replace the olefins plant for benzene production	
3	Propylene oxide (P1) Propylene glycol (P2) Methanol-to-aromatics (MtA) CO2-to-methanol via hydrogeneration (CH)	To replace fossil-based methanol and butane	
4	MTBE (M) Propylene oxide (P1) methanol-to-aromatics (MtA) Biomass-to-isobutylene (BI)	To replace fossil-based isobutylene and butane	
5	Olefins (O) Ethylbenzene (E) Styrene monomer (S) Methanol-to-aromatics (MtA) Biomass-to-olefins (MtO)	To replace fossil-based ethylene and propylene	

Table 7. Potential replacement and integration of ACS-based plants in the Port of Rotterdam for portfolio optimization assessment. *C2E, Ethylene; MeOH, Methanol; BZ, Benzene; PO, Propylene oxide; PGME, Propylene glycol methyl ether; TBA, Tert butyl alcohol; i-C4E, Isobutylene; C3E, Propylene; EB, Ethylbenzene. ** The role of integrating plastic waste pyrolysis for achieving full defossilization is analyzed separately in Section S.3 in supplementary materials B for assessment of ACS-based naphtha replacement.

ensuring a feasible starting point. The convergence criteria, i.e. optimality tolerance and constraint tolerance are both set to 10^{-6}.

Scenario 1: Replacement of fossil-based olefins for ethylene production

The olefins plant (also known as the naphtha steam cracker) is a critical plant at the beginning of most value chains within the entire cluster of the Port of Rotterdam. Therefore, its defossilization has a significant impact on the overall cluster. During the cracking process, a range of lower hydrocarbons is produced, among which ethylene and benzene are the most prominent in terms of both volume and importance. In this scenario, the potential ACS-based plants for replacing the olefins plant in ethylene production are studied in the context of investment decision-making.

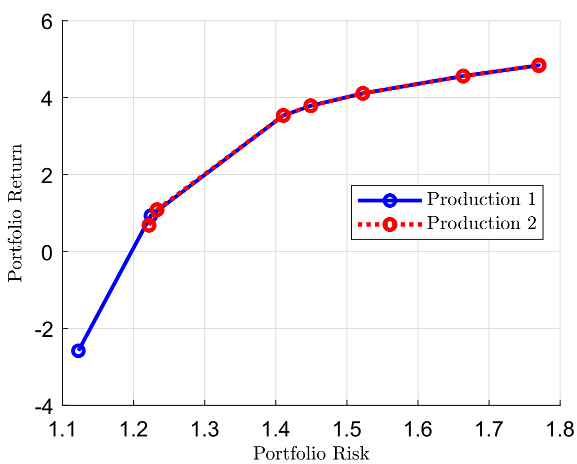
For the optimization model, two constraints regarding the total investment and demand production of ethylene are defined as follows:

$$\sum_{n=1}^{3} c_n\, T_n \leq 1.05\, \max(T_1, T_2, T_3) \tag{20a}$$

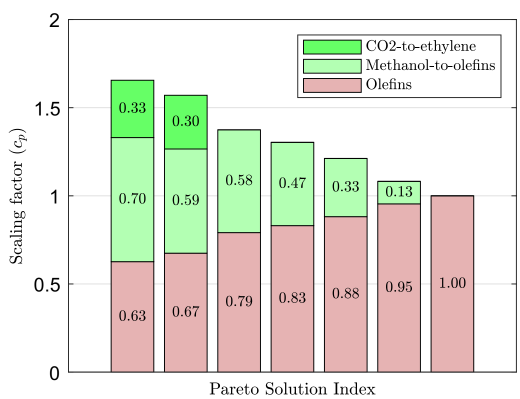
$$\sum_{n=1}^{3} c_n\, P_n = D_r \tag{20b}$$

where the first constraint ensures that the total investment does not exceed the capital cost of the most expensive stand-alone plant among the three considered options (as this scenario is replacement), and the second constraint guarantees that the required ethylene production is met (according to (9d) and data in Table 2). To define the ethylene production demand, two values are used: $D_r = 53.55\frac{\mathrm{kt}}{\mathrm{month}}$ (production 1, which is the sum of productions of mathanol-to-olefins and CO2-to ethylene plants at their maximum production capacities), and $D_r = 73.18\frac{\mathrm{kt}}{\mathrm{month}}$ (production 2, which is the ethylene production of olefins plant at its maximum production capacity). These two values are used to investigate the impact of the production constraint on the optimization results. Furthermore, since this scenario is the replacement of a fossil-based plant with ACS-based alternatives, the minimum and maximum scaling factors for all options are set to zero and one, respectively.

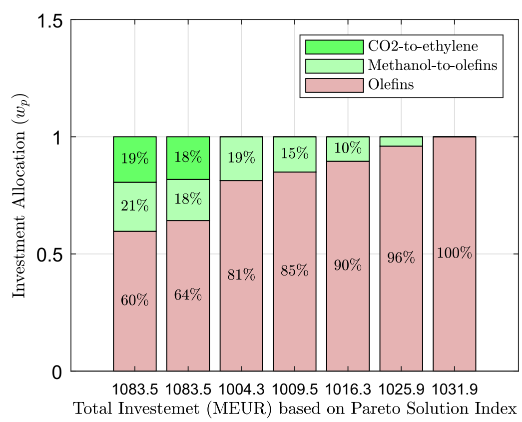
The results based on the market-based economic parameters are shown in Fig. 2. As shown in Fig. 2a, the maximum return is achieved at $R = 4.84, \sigma = 1.77$, which corresponds to the stand-alone return and risk of the olefins plant. This can also be seen in Figs. 2b and c (the rightmost bars), where both the scaling factor and the total investment (in terms of distribution and value) are allocated solely to the olefins plant. When the ACS-based options are included in the portfolio configuration, the overall return decreases due to the negative RoIs of both methanol-to-olefins and CO2-to-ethylene plants. The optimization model configures the portfolio in such a way that reductions in RoI come along with corresponding reductions in investment risk. Consequently, full defossilization does not emerge as an optimal selection due to the negative RoI and high risk associated with ACS-based plants. As can be seen in Fig. 2a, the lowest RoI and risk for Production 1 and Production 2 occur at $R = 0.68, \sigma = 1.22$ and $R = -2.58, \sigma = 1.12$, respectively. This difference arises because, with a lower ethylene production constraint, the optimization model can fully meet the requirement using only ACS-based options by summing their maximum production capacities. In contrast, when the ethylene production constraint is set to a higher value, partial involvement of the olefins plant becomes inevitable. This increases the overall RoI due to the positive return associated with the olefins plant. Therefore, with the higher value for the ethylene production constraint (i.e. $73.13\frac{\mathrm{kt}}{\mathrm{month}}$), we still have a positive return by involvement of 0.33, 0.70,



(a) The return-risk relationship for two ethylene production levels.



(b) Scaling factors corresponding to return-risk relationships for the ethylene production 2.

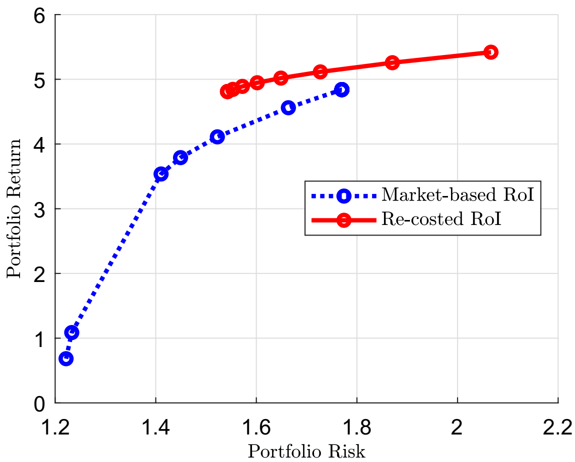


(c) Investment distributions corresponding to return-risk relationships for the ethylene production 2.

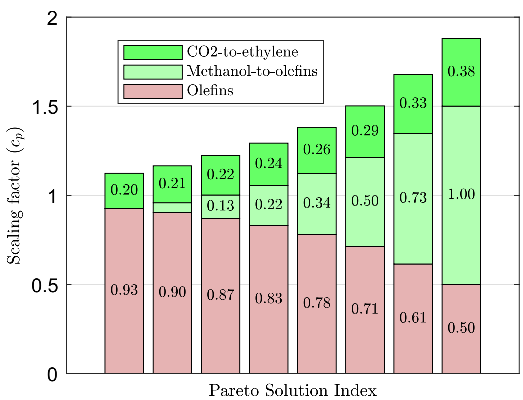
Fig. 2. Scenario 1: Replacement of olefins for ethylene production with methanol-to-olefins and electrochemical reduction of CO2; Market-based economic parameters are used.

and 0.63 of the maximum production capacities of CO2-to-ethylene, methanol-to-olefins, and olefins plants, respectively (as shown in Fig. 2b), which highlights 37% defossilization in total. Total investment is based on 1.05 times that of the stand-alone olefins plant (i.e. 1083.5 M€). The investment distributions and the corresponding scaling factors are shown in Figs. 2b and c (ordered from right to left, from the highest to the lowest RoI, according to the return-risk relationship).

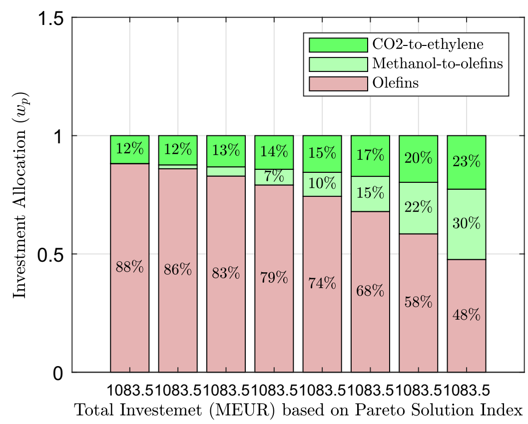
For the second simulation, we use the re-costed economic parameters to investigate the transition, assuming that ACS-based plants yield positive RoIs. Constraints are assumed to be the same as in the previous simulation, but only for the higher ethylene production capacity, i.e., $73.18\frac{\text{kt}}{\text{month}}$. The results are shown in Fig. 3. As can be seen in Fig. 3a, the relative RoIs are higher than in the previous case with the market-based economic parameters. The relative risk also increases, as the inclusion of ACS-based plants, which brings their higher RoIs to the portfolio, involves correspondingly higher investment risks into the portfolio selection. The standard deviations of the ACS-based options rise under the re-costed economic parameters. The highest return occurs at $R = 5.42, \sigma = 2.07$ with scaling factors of 0.50, 1.00, and 0.38 for the olefins, methanol-to-olefins, and CO2-to-ethylene plants, respectively (see the rightmost bar in Fig. 3b). The total investment also does not exceed 1083.5 M€ across various portfolio selections, as shown in Fig. 3c. Moreover, the lowest RoI under the re-costed parameters is nearly equal to the highest RoI of the previous case, i.e., $R = 4.81$, but with a lower risk, i.e., $\sigma = 1.54$, and unlike the market-based prices, this portfolio is not 100% fossil-based and includes the CO2-to-ethylene plant in the portfolio selection. In contrast to the previous case, at lower RoIs, the CO2-to-ethylene plant becomes more attractive among the two options of ACS-based plants due to its higher RoI and lower risk. However, as the portfolio shifts toward higher RoIs, the optimization model tends to include more production from the methanol-to-olefins plant, since it has a lower capital cost than the CO2-to-ethylene plant (see Fig. 3b and c, from left to right bars, corresponding from the lowest to the highest RoI).



(a) The return-risk relationship for market-based and re-costed economic parameters.



(b) Scaling factors corresponding to return-risk relationships.



(c) Investment distributions corresponding to return-risk relationships.

Fig. 3. Scenario 1: Replacement of olefins for ethylene production with methanol-to-olefins and electrochemical reduction of CO2; Re-costed economic parameters are used.

Besides the detailed investigation discussed above, the following general observations can also be made for the replacement of the olefins plant for ethylene production with methanol-to-olefins and electrochemical reduction of CO2:

- From an investment point of view, full defossilization is not achieved for either the market-based or re-costed economic parameters.
- Even with the market-based economic parameters, defossilization can be applied to some extent by incorporating partial production capacities of both CO2-to-ethylene and methanol-to-olefins plants.
- Using re-costed economic parameters meaning that a premium is allocated to the ACS-based plants,, at the extreme case of defossilization, we can reach almost 5 times the RoI in the portfolio during the transition, but this is subject to governmental financial supports.
- Methanol-to-olefins is relatively more attractive for investment in the transition from fossil-based feedstocks in this scenario than CO2-to-ethylene.

Scenario 2: Replacement of fossil-based olefins for benzene production

Similar to Scenario 1, the olefins plant is intended to be replaced, but in this scenario, it is for benzene production. The potential ACS-based plants to fulfill the required benzene demand for the cluster are methanol-to-olefins and methanol-to-aromatics, with the latter offering approximately 4 times higher benzene production (see Table 2). Two constraints for the total investment and the required production demand are defined as follows:

$$\sum_{n=1}^{3} c_n\, T_n \leq 1.05\ \max(T_1, T_2, T_3) \tag{21a}$$

$$0.78\, c_1\, P_1 + 0.25\, c_2\, P_2 + c_3\, P_3 = D_r \tag{21b}$$

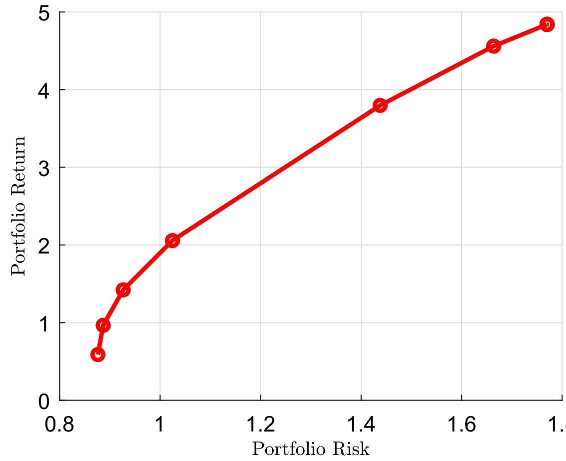
where the second constraint is the extended form of (9d), based on the stoichiometric parameters in Table 2, for olefins (denoted as 1), methanol-to-olefins (denoted as 2), and methanol-to-aromatics (denoted as 3). The production demand, D_r, is set to $57.08\frac{\text{kt}}{\text{month}}$, based on the maximum production capacity of the olefins plant as mentioned in Table 1. This value is also approximately equal to the total benzene that can be produced from the two ACS-based plants.

The first simulation is based on the market-based economic parameters. The results are shown in Fig. 4. As expected and similar to the previous scenario, the maximum return is achieved at $R = 4.84, \sigma = 1.77$, which corresponds to 100% fossil-based feedstocks (see Fig. 4aand the rightmost bar in Fig. 4b). The transition to non-fossil feedstocks reduces the RoI of the portfolio, as the RoIs of both methanol-to-olefins and methanol-to-aromatics are negative (see Table 3). However, a positive portfolio RoI is still achievable with the highest possible level of defossilization i.e. 24% at $R = 0.59, \sigma = 0.88$. This is also subject to the highest investment value, i.e., 1639.6 M€, as shown by the leftmost bar in Fig. 4c. As can also be seen in Fig. 4c, during the transition (from the right bar to the left bar), the portfolio selection tends to include methanol-to-olefins. However, at some point, the inclusion of methanol-to-aromatics becomes more attractive due to its production capacity being almost four times higher than that of the other ACS-based plant. The reason methanol-to-aromatics is not included at the lowest level of defossilization is its significantly higher capital cost compared to methanol-to-olefins (capital costs are 2796.1 M€ and 322.04 M€, respectively). Another reason is related to the correlation factors between olefins and methanol-to-aromatics, and olefins and methanol-to-olefins. Based on Table 4, both correlations are negative, but the correlation between olefins and methanol-to-aromatics is more strongly negative, making methanol-to-aromatics less attractive to include in the portfolio selection, unless methanol-to-olefins production cannot meet the demand.

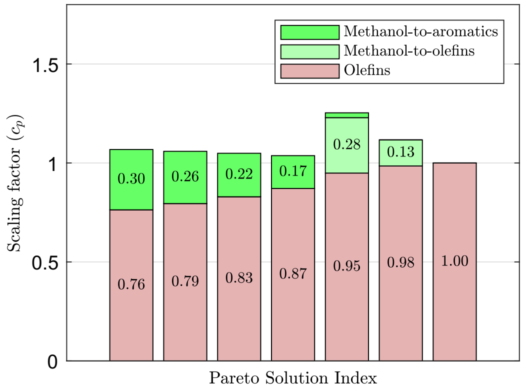
The second simulation is based on the re-costed economic parameters. The results are shown in Fig. 5. As can be seen in Fig. 5a, although the relative RoIs of the various portfolios are higher than those based on the market-based economic parameters, the highest achievable RoI occurs at $R = 4.87, \sigma = 1.84$, which is not significantly higher than the RoI obtained with the market-based parameters. This is because the re-costed RoI of methanol-to-aromatics, which can produce a large amount of benzene, is still low ($R = 1.85$), making the transition less attractive. This is also the reason why a relatively high level of defossilization (11% and 14%) occurs only at the two extremes of the RoI spectrum. According to Fig. 5b, these occur at the rightmost and leftmost bars, corresponding to the predominant inclusion of methanol-to-aromatics and methanol-to-olefins, respectively. However, the scaling factor of methanol-to-olefins is much higher than that of methanol-to-aromatics, due to differences in the amount of benzene produced. In terms of total investment for these two transition cases, although full capacity production of methanol-to-olefins is required in the one of these portfolios, the total investment remains lower than that of the alternative case, with an investment amount of 1235.5 M€ (see Fig. 5c).

In general, the following observations can be drawn regarding the replacement of olefins for benzene production:

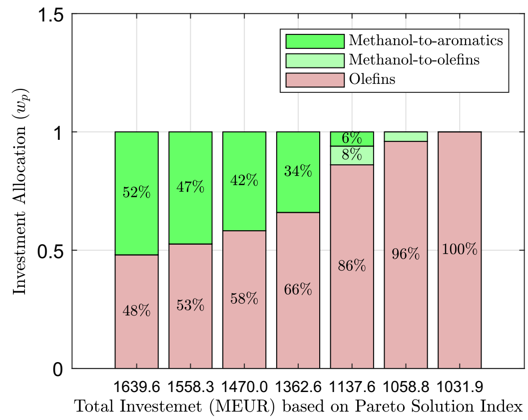
- Methanol-to-aromatics is a capital-intensive technology, which makes it less attractive for the optimization model to include it in the portfolio under both market-based and re-costed economic parameters.
- With the market-based economic parameters, defossilization can be applied to some extent by incorporating partial capacities of both methanol-to-aromatics and methanol-to-olefins plants.
- Using re-costed economic parameters, the transition remains unattractive, and the level of defossilization is still low, indicating the need for greater governmental financial support.



(a) The return-risk relationship.



(b) Scaling factors corresponding to return-risk relationships.



(c) Investment distributions corresponding to return-risk relationships.

Fig. 4. Scenario 2: Replacement of olefins for benzene production with methanol-to-olefins and methanol-to-aromatics; Market-based economic parameters are used.

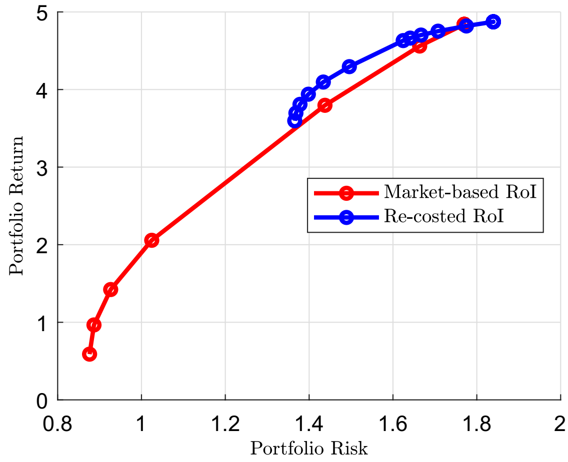
- Methanol-to-olefins is a more attractive investment option for the transition from fossil-based feedstocks, as it can contribute a relatively acceptable share to both ethylene and benzene production.

Scenario 3: Integration of methanol-to-aromatics and CO2-to-methanol via hydrogeneration in PGME value chain

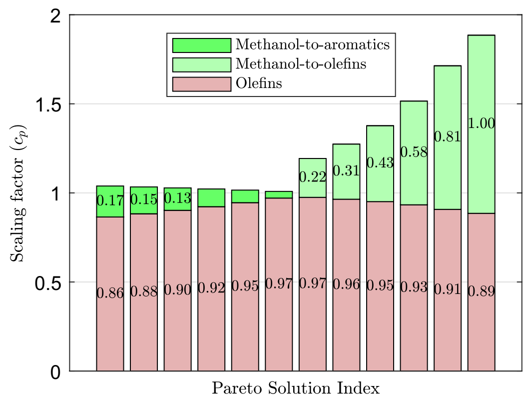
Propylene oxide and propylene glycol are two plants operated by one company at the Port of Rotterdam. These plants represent a value chain, where they are interconnected, and propylene oxide is shared between them for the production of PGME. In addition to PGME, other products such as tert-butyl alcohol and excess propylene oxide are also produced and shared with other plants in the cluster. To defossilize this production line, two feedstocks, i.e. butane (fed to the propylene oxide plant) and methanol (fed to the propylene glycol plant), can be sourced from the outputs of two ACS-based plants: methanol-to-aromatics and CO2-to-methanol via hydrogenation, respectively. Therefore, this scenario analyzes the integration of these two ACS-based plants to investigate investment directions.

To formulate the optimization model for this scenario, the presence of the propylene oxide and propylene glycol plants is fixed with scaling factor of one, while the lower and upper limits of the scaling factors for the methanol-to-aromatics and CO2-to-methanol via hydrogenation plants are set to 0 and 1, respectively. Another constraint regarding total investment is also included. Unlike the replacement scenarios, this scenario represents the integration of additional plants. Therefore, the total investment constraint is written as the sum of the total capital costs of all potential options, as follows:

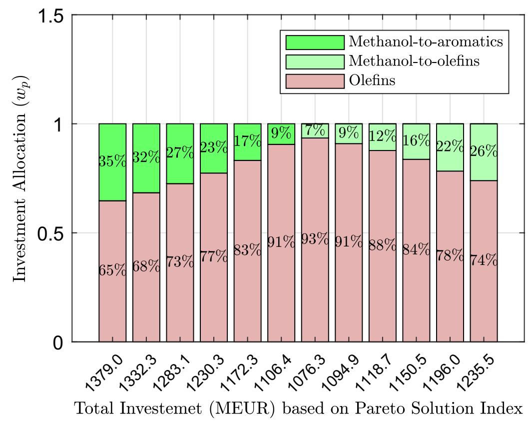
$$\sum_{n=1}^{4} c_n\, T_n \leq 1.05\ \mathrm{sum}(T_1, T_2, T_3, T_4) \tag{22}$$



(a) The return-risk relationship for market-based and re-costed economic parameters.



(b) Scaling factors corresponding to return-risk relationships.



(c) Investment distributions corresponding to return-risk relationships.

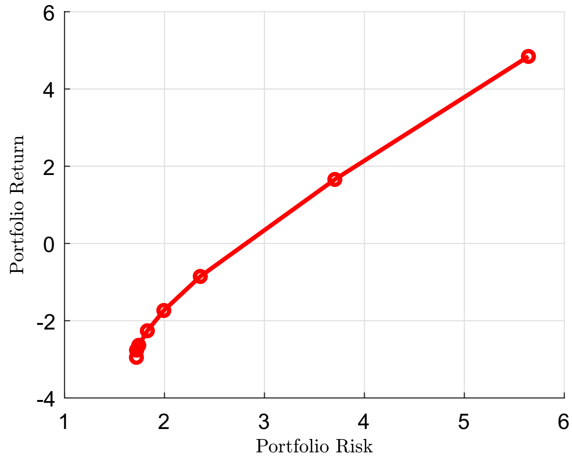
Fig. 5. Scenario 2: Replacement of olefins for benzene production with methanol-to-olefins and methanol-to-aromatics; Re-costed economic parameters are used.

The results based on the market-based economic parameters are shown in Fig. 6. As can be seen in Fig. 6a, it can be observed that the transition from fossil-based feedstocks requires a large amount of investment, ranging from 213.1 M€ to 3045.4 M€. The majority of the investment during this transition is allocated to the methanol-to-aromatics plant, primarily due to its high capital cost, as previously mentioned.

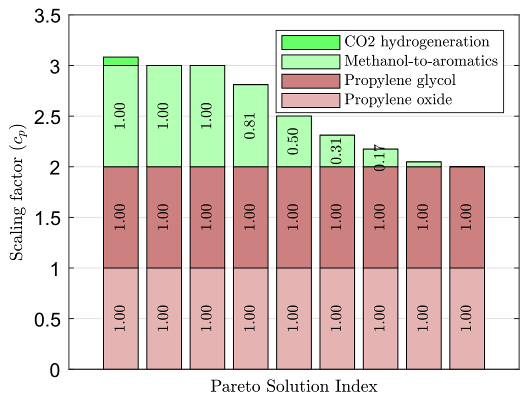
For the second simulation, based on the re-costed economic parameters, the results are shown in Fig. 7. As can be seen in Fig. 7a, the RoI and standard deviation of the various portfolios do not vary significantly, which makes the investment decision straightforward, favoring the portfolio that offers the highest level of defossilization. This is because the inclusion of the propylene oxide and propylene glycol plants is fixed, and the positive re-costed RoIs of the methanol-to-aromatics and CO2-to-methanol via hydrogenation plants make them attractive candidates for including into the portfolio. The highest level of defossilization of butane occurs at $R = 2.36, \sigma = 1.56$, with 0.13 of the maximum production capacity of methanol-to-aromatics, and 0.48 of the maximum production capacity of CO2-to-methanol via hydrogenation (see the mostleft bar in Fig. 7b). This corresponds to an investment of 769.7 M€, with an allocation of 46% for methanol-to-aromatics, and 27% for CO2-to-methanol via hydrogenation (see the mostleft bar in Fig. 7c). Moreover, CO2-to-methanol via hydrogenation is able to fulfill 100% of the demand for the propylene glycol plant, as the required amount is relatively low, i.e. $3.06\,\frac{\text{kt}}{\text{month}}$ (see the mostright bar in Fig. 7b).

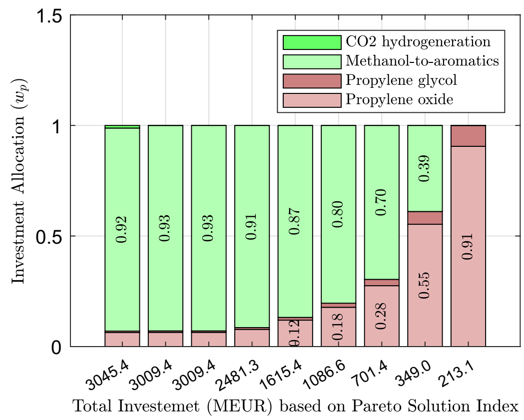
Based on the aforementioned discussion, the following key points regarding the integration of methanol-to-aromatics and CO2 hydrogenation into the PGME value chain can be highlighted:

- The transition from fossil-based feedstocks is not attractive for investment using market-based economic parameters; however, it can be profitable with re-costed prices.
- With the re-costed economic parameters, partial deffossilization is economically feasible by integrating both methanol-to-aromatics and CO2-to-methanol via hydrogenation.



(a) The return-risk relationship.





(b) Scaling factors corresponding to return-risk relationships subject to the methanol constraint.

(c) Investment distributions corresponding to return-risk relationships subject to the methanol constraint.

Fig. 6. Scenario 3: Integration of methanol-to-aromatics and CO2-to-methanol via hydrogeneration in PGME value chain; Market-based economic parameters are used.

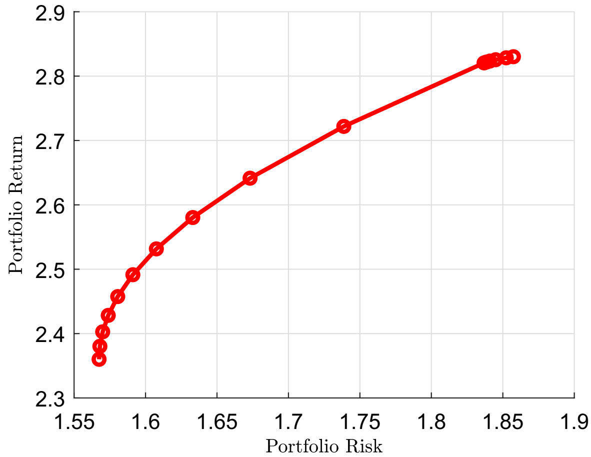
Scenario 4: Integration of methanol-to-aromatics and biomass-to-isobutylene in MTBE value chain

This scenario investigates the MTBE value chain. Here, the propylene oxide plant shares tert-butyl alcohol with the MTBE production plant. To some extent, this can be defossilized by methanol-to-aromatics fulfilling the butane requirement, as in the previous scenario, and biomass-to-isobutylene supplying isobutylene for the MTBE production plant. The latter integration is suggested by Stepchuk et al.[11], which also assessed the impacts of deploying bio-based isobutene for MTBE production at both the process and cluster levels. For this scenario, the presence of the propylene oxide and MTBE plants is fixed, while the scaling factors for the methanol-to-aromatics and biomass-to-isobutylene plants are determined by the optimization model. A constraint regarding total investment is included as follows:

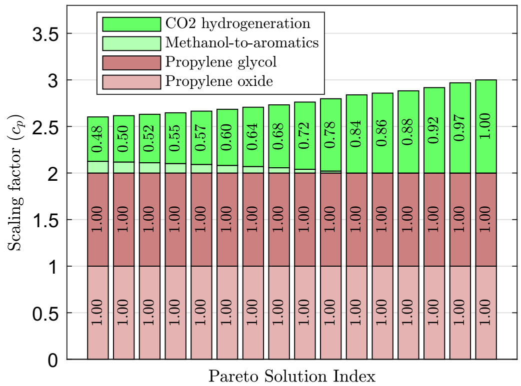
$$\sum_{n=1}^{4} c_n\,T_n \leq 1.05\,\max(T_1, T_2, T_3, T_4) \tag{23}$$

where the numbers 1 to 4 represent MTBE, propylene oxide, methanol-to-aromatics, and biomass-to-isobutylene plants, respectively.

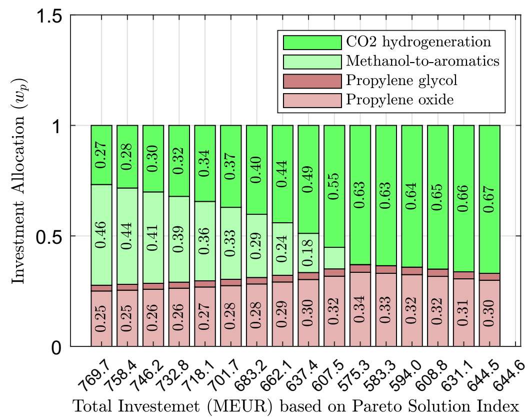
The results for the market-based economic parameters are shown in Fig. 8. As can be seen, the inclusion of biomass-to-isobutylene is chosen with the maximum production capacity for all portfolios at the Pareto front. which meets the the isobutylene demand of the MTBE plant and the extra amount is considered as the product to sell. As methanol-to-aromatics is included in the portfolio, the portfolio RoI decreases due to the negative RoI of this plant. Therefore, the highest level of defossilization occurs at the lowest RoI, i.e., $R = -0.34, \sigma = 1.14$, with full defossilization of isobutylene and 75% of butane by including 0.50 of the maximum production capacity of methanol-to-aromatics (see the leftmost bar in Fig. 8b). This also corresponds to the highest investment value



(a) The return-risk relationship.



(b) Scaling factors corresponding to return-risk relationships subject to the methanol constraint.



(c) Investment distributions corresponding to return-risk relationships subject to the methanol constraint.

Fig. 7. Scenario 3: Integration of methanol-to-aromatics and CO2-to-methanol via hydrogeneration in PGME value chain; Re-costed economic parameters are used.

of 3632.2 M€ based on Fig. 8c, with investment allocation of 55% and 38% for biomass-to-isobutylene and methanol-to-aromatics, respectively.

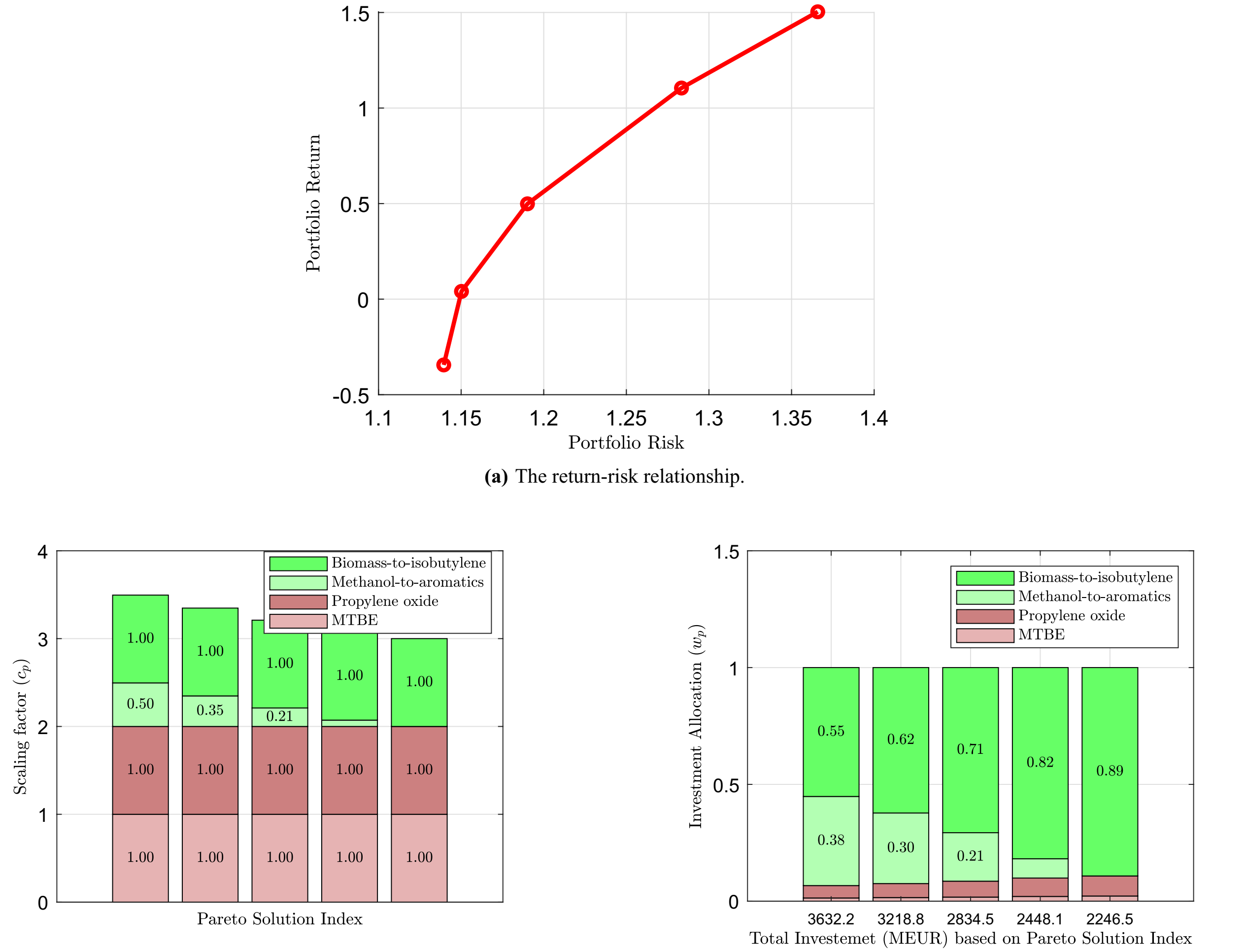
The results based on the re-costed economic parameters are shown in Fig. 9. As can be seen in Fig. 9a, RoIs of the various portfolios increase due to the re-costed RoIs of the considered plants, and the transition from fossil-based feedstocks based on the re-costed economic parameters is similar to the market-based economic parameters, i.e., lower RoI corresponds to a higher level of defossilization. This is because the economic parameters for the fixed plants are still more favorable than those of the ACS-based plants, which highlights that even if the re-costed economic parameters of ACS-based options shift towards positive values, they still remain lower than the market-based of the fossil-based ones to be selected in the portfolios of higher RoIs. While the overall RoIs are increased, but the percentage of defossilization is relatively lower than market-based simulation, which shows re-costed prices in this scenario is only favorable for the return of investment, not defossilization.

Therefore, the following highlights regarding the integration of methanol-to-aromatics and biomass-to-isobutylene into the MTBE value chain can be pointed out:

- The transition from fossil-based feedstocks is not very attractive for investment using re-costed economic parameters.
- A relatively high deffossilization based on both market-based and re-costed economic parameters are achievable in this scenario.

Scenario 5: Integration of methanol-to-olefins and methanol-to-aromatics

This scenario investigates the portfolio of a value chain with more plants. It is also aligned with Scenarios 1 and 2, but considers both ethylene and benzene production simultaneously by replacing the olefins plant through the integration of methanol-to-olefins and methanol-to-aromatics. Therefore, the ethylbenzene production plant and the styrene production plant, which are connected through the exchange of ethylbenzene, are considered in



(a) The return-risk relationship.

(b) Scaling factors corresponding to return-risk relationships.

(c) Investment distributions corresponding to return-risk relationships.

Fig. 8. Scenario 4: Integration of methanol-to-aromatics and biomass-to-isobutylene in MTBE value chain; Market-based economic parameters are used.

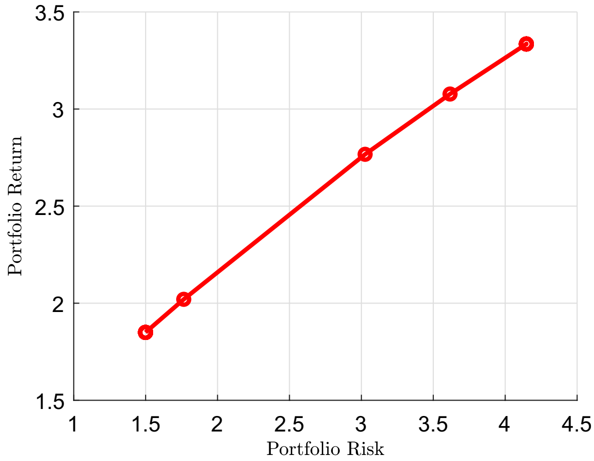
this scenario in addition to the olefins plant that supplies ethylene, propylene, and benzene to both. To replace these resources, methanol-to-aromatics (as the main benzene provider) and methanol-to-olefins (as the main ethylene and propylene provider) are potential ACS-based plants. To formulate the optimization problem, in addition to the investment constraint (expressed as the summation of the capital costs of the fixed plants and the maximum capitals of the replacement options) a constraint on benzene production is also included as follows:

$$\sum_{n=1}^{5} c_n\, T_n \leq 1.05\ (T_1 + T_3 + \max(T_2, T_4, T_5)) \tag{24a}$$

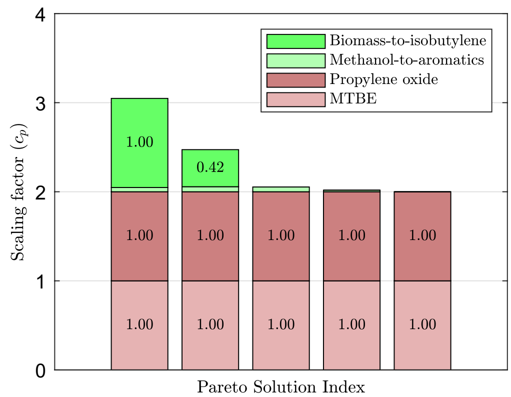
$$-\,0.75\, c_1\, P_1 + 0.78\, c_2\, P_2 + 0.25\ c_4\, P_4 + c_5\, P_5 = 0 \tag{24b}$$

in which the numbers 1 to 5 represent ethylbenzene, olefins, styrene, methanol-to-aromatics, and methanol-to-olefins, respectively. The reason for including the second constraint is that benzene is entirely closed within this value chain, with no external sales or exchanges with other companies within the cluster. Therefore, we impose this constraint to ensure that the internal demand for benzene is totally met.

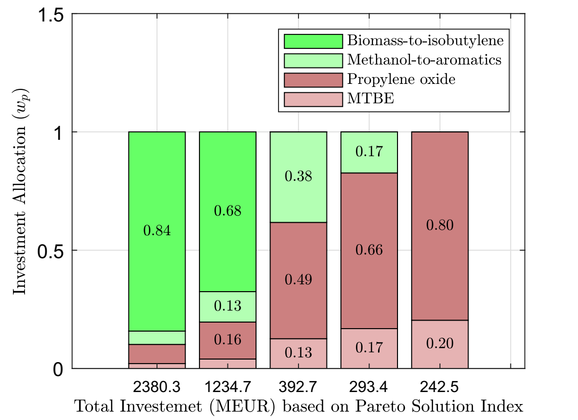
The results based on the market-based economic parameters are shown in Fig. 10. Since the RoIs of the ethylbenzene and styrene plants are negative, the optimization model tends to include the olefins plant as the only positive RoI plant to compensate for the return of the portfolio instead of selecting ACS-based alternatives. Moreover, between the two available ACS-based options, methanol-to-olefins has a higher standard deviation; therefore, it is less likely to be included in lower RoI portfolios. If the model is not explicitly constrained to integrate it, methanol-to-olefins is not selected in any portfolio (the red line in Fig. 10a). However, by imposing a minimum integration constraint of at least 0.20 of the maximum production of methanol-to-olefins (implemented via a lower bound on its scaling factor in the optimization model) the relative RoI decreases as expected (the blue line in Fig. 10a). The inclusion of methanol-to-aromatics also varies between 0 and 0.15



(a) The return-risk relationship.



(b) Scaling factors corresponding to return-risk relationships.



(c) Investment distributions corresponding to return-risk relationships.

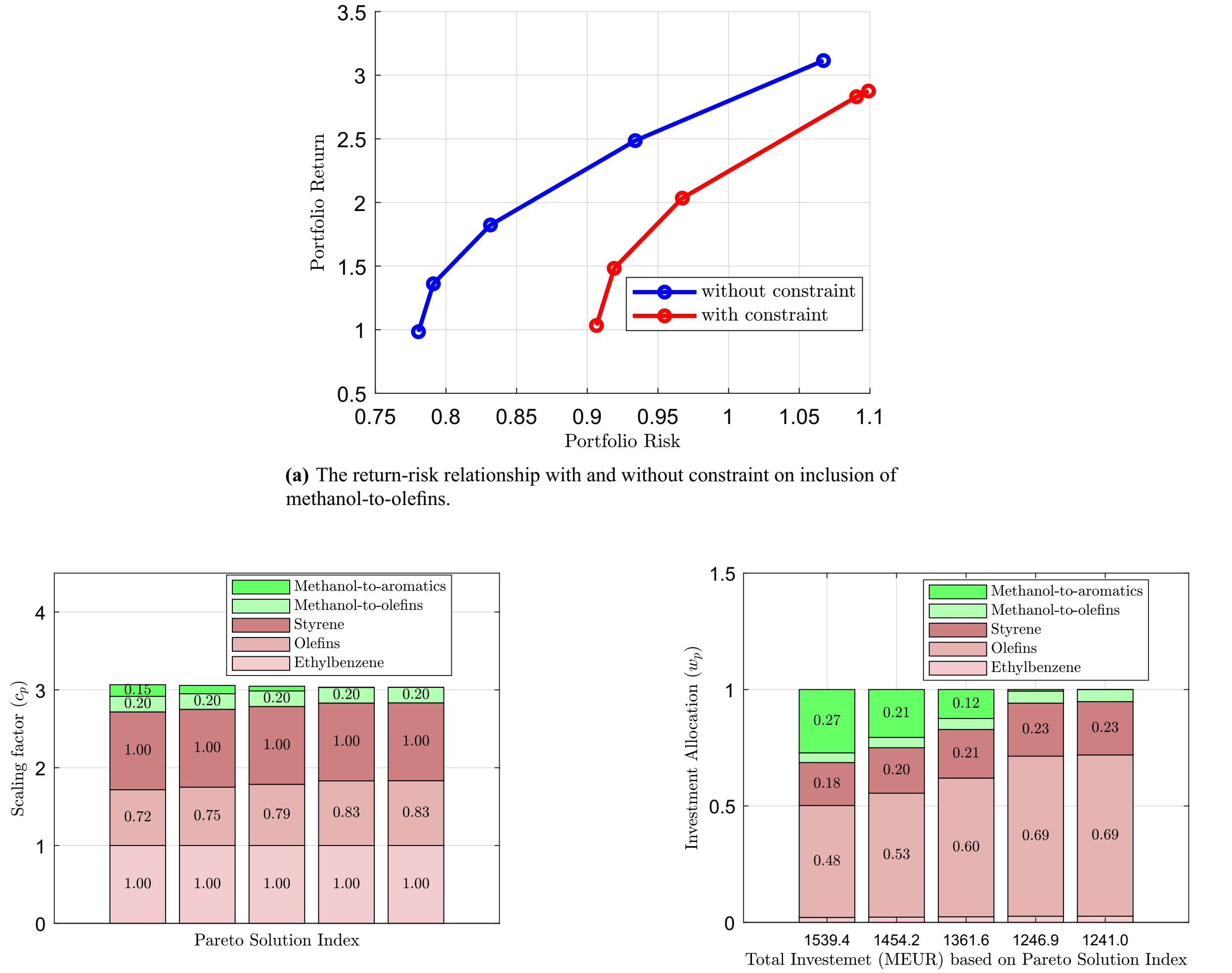
Fig. 9. Scenario 4: Integration of methanol-to-aromatics and biomass-to-isobutylene in MTBE value chain; Re-costed economic parameters are used.

of the maximum production capacity, resulting to the reduction in portfolio return and also increasing total investment (from right to left bars in Fig. 10c).

Using the re-costed economic parameters, the results are shown in Fig. 11. These results are fully consistent with those obtained under the re-costed economic parameters in Scenario 2. Therefore, from the lowest to the highest RoI, the inclusion of methanol-to-aromatics is initially more attractive, but at a certain point, it shifts toward the inclusion of methanol-to-olefins (from left to right bars in Fig. 11b) with full production capacity of methanol-to-olefins at $R = 3.99, \sigma = 1.63$. Furthermore, similar to Scenario 2, a relatively high level of defossilization occurs at both extremes of the RoI spectrum. This increase is due to the inclusion of the ethylbenzene and styrene plants and their correlation characteristics, i.e. their negative correlation with the negative RoI of the ethylbenzene plant and their positive correlation with the positive RoI of the styrene plant. This highlights the significance of the availability of multiple viable options when constructing an investment portfolio. A decision between the two highest levels of defossilization can also be made in favor of the inclusion of methanol-to-aromatics, as it requires a relatively lower investment cost compared to the alternative case, i.e. 1403.9 M€ (see the rightmost and leftmost bars in Fig. 11c

Taking the aforementioned technical discussions into account, the following notes can also be drawn for the integration of methanol-to-olefins and methanol-to-aromatics in a medium-stage value chain:

- The fixed inclusion of plants in a longer value chain impacts the defossilization from an investment point of view, based on the economic characteristics of those fixed plants; for instance, less defossilization based on re-costed economic parameters in comparison with market-based ones, while increasing return.
- Methanol-to-olefins is still a more attractive investment option for the transition from fossil-based feedstocks, as it can contribute a relatively acceptable share to both ethylene and benzene production with a cheaper capital cost.



(a) The return-risk relationship with and without constraint on inclusion of methanol-to-olefins.

(b) Scaling factor corresponding to return-risk relationships with constraint on inclusion of methanol-to-olefins.

(c) Investment distributions corresponding to return-risk relationships with constraint on inclusion of methanol-to-olefins.

Fig. 10. Scenario 5: Integration of methanol-to-olefins and methanol-to-aromatics in a value chain; Market-based economic parameters are used.

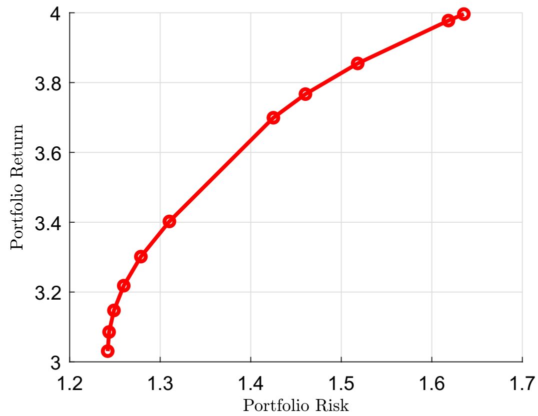
$\epsilon-$constraint method for distributed solutions

The above results are derived based on the original solution method, the weighted-sum approach, as discussed by Lhabitant[23]. As can be seen in the obtained results, the method is somewhat sensitive to weight changes, which might result in some gaps in the return-risk trade-offs. Therefore, to provide a more distributed solution and mitigate the arbitrariness of the weight selection, the results of Scenario 1 (representing a short value chain) and Scenario 5 (representing a long value chain) are re-derived based on the ϵ-constraint method, given in (10a)–(10e). The bound on ϵ varies between the minimum possible risk and the maximum possible risk. The minimum risk is obtained by solving a single-objective optimization problem focused solely on risk minimization. Conversely, the maximum risk is obtained by solving a single-objective optimization problem focused on return maximization. Therefore, a distributed Pareto front can be obtained by varying the bound of risk.

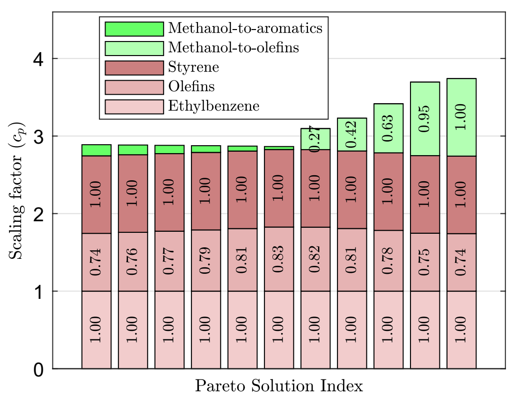
As Fig. 12 shows, the risk-return trade-off curve obtained using the ϵ-constraint method is more distributed, although the two extreme points of the spectrum remain unchanged compared to the weighted-sum method. In other words, changing to the ϵ-constraint solution method does not change the maximum possible defossilization. However, it provides investors with more intermediate options to choose from. These additional options can also be observed from, scaling factors and the corresponding investment distributions, shown in Fig. 12. It should also be noted that the conclusion drawn from the primary solution method remains valid, i.e. the direction of ACS-based technology inclusion in the portfolio is unchanged. The $\epsilon-$constraint method solution method can only offer more intermediate options to investors interested in such trade-offs.

A holistic discussion of the transition from fossil-based feedstocks from an investment perspective in practice and future directions

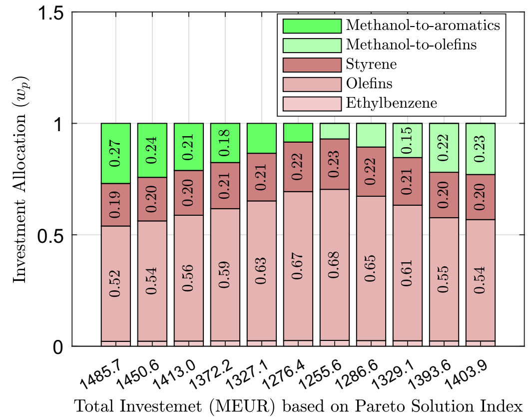
Practical challenges for the transition from fossil-based feedstocks have been identified for two case studies at both process and cluster levels in the Port of Rotterdam by Manalal et al.[12] and Stepchuk et al.[11]. These challenges



(a) The return-risk relationship.



(b) Scaling factor corresponding to return-risk relationships.



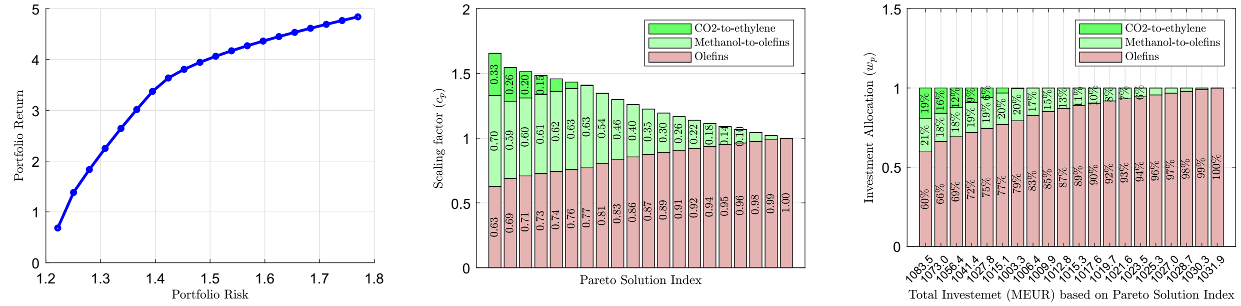
(c) Investment distributions corresponding to return-risk relationships.

Fig. 11. Scenario 5: Integration of methanol-to-olefins and methanol-to-aromatics in a value chain; Re-costed economic parameters are used.

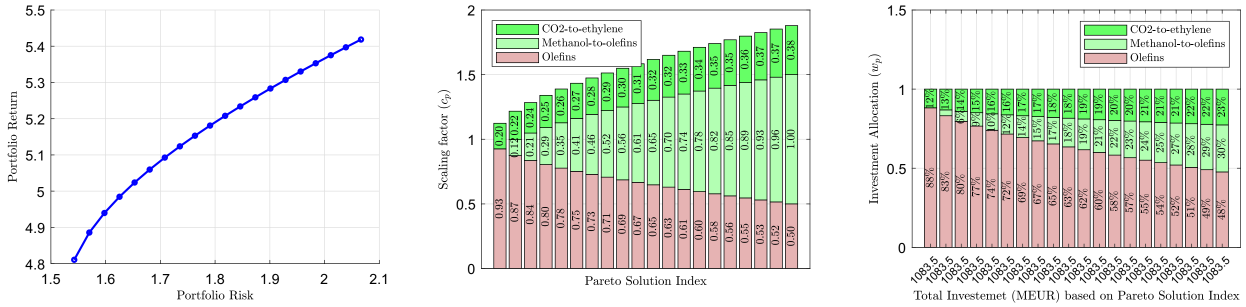
mainly include additional utility requirements such as electricity and water supply, significantly larger bare land needed for deploying ACS-based plants, and downstream implications due to major changes in (by-)product outputs. However, in this study, a further investigation has been conducted from a decision-maker's perspective to highlight the investment challenges associated with such a transition in the Port of Rotterdam. Therefore, five cases have been analyzed based on the proposed optimization model to investigate the profitability and further feasibility of the transition by identifying optimal portfolios. Based on the aforementioned explorations and analyses, the following implications regarding the transition in the Port of Rotterdam can be noted:

- As calculated, stand-alone ACS-based plants exhibit negative RoIs (sometimes with high risk), making their full deployment within the cluster economically unreasonable. This highlights the need for a gradual replacement and integration with adjusted capacities to ensure investment viability (as done in this paper).
- According to recent historical market prices, shifting towards ACS-based plants, which are highly capital-intensive, reduces the RoI of the portfolios (in some cases even resulting in negative values), consequently preventing full defossilization and highlighting the need for governmental financial supports.
- Utilizing the allocation method based on the bare minimum price and the added values of fossil-based counterparts to re-cost the (by-)products of ACS-based plants can make defossilization somewhat attractive for investment. However, it still requires substantial governmental subsidies.
- Reaching to full defossilization based on both market-based and re-costed prices is not totally economically reasonable (see Table 8 and Table S.2 in supplementary materials B). As it is in line with other environmental and techno-economic analyses, a reconsideration including all the aspects together may be required.

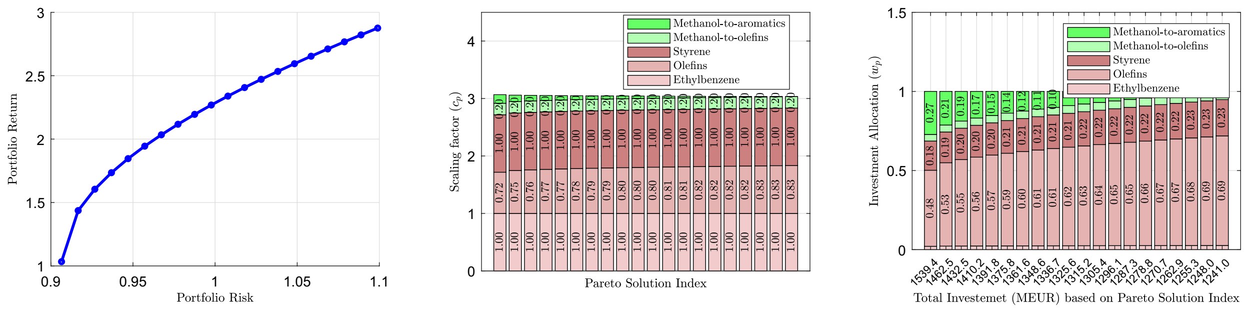
Therefore, the transition from fossil-based feedstocks faces practical investment challenges, mainly related to adjusting the current capacities of fossil-based plants and providing governmental subsidies to compensate for profitability gaps.



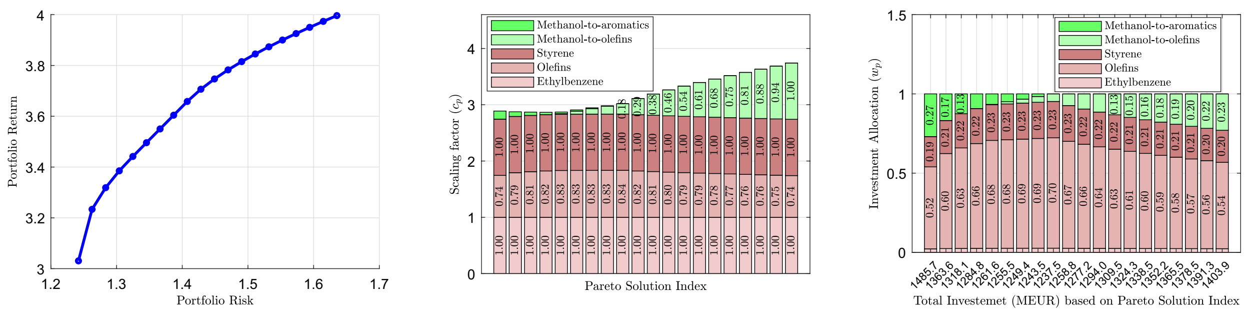
(a) Scenario 1, market-based prices.



(b) Scenario 1, re-costed prices.



(c) Scenario 5, market-based prices.



(d) Scenario 5, re-costed prices.

Fig. 12. Solutions of the $\epsilon-$constraint method for Scenarios 1 and 5.

Conclusions

To unlock the potentials and challenges of transitioning from fossil-based feedstocks in an industrial cluster, an optimization model is proposed based on the modern portfolio theory. The outputs of the MPT-based optimization investigate the economic angles of this transition and provide investment planning by selecting optimal portfolios from existing fossil-based plants and potential ACS-based alternatives. The optimal portfolio configurations are based on the maximization of RoI while minimizing risk by fully allocating the investment among potential portfolio options and determining the corresponding production capacities. Five scenarios

Scenario	Economic parameters	Return-risk	Defossilization percentage
Scenario 1	Market-based	(0.68,1.22)	37% naphtha
	Re-costed	(5.42,2.07)	50% naphtha
Scenario 2	Market-based	(0.59,0.88)	24% naphtha
	Re-costed	(3.60,1.36)	14% naphtha
Scenario 3	Market-based	(-2.95,1.72)	100% butane 10% methanol
	Re-costed	(2.83,1.85)	100% methanol
Scenario 4	Market-based	(-0.34,1.40)	100% isobutylene 50% butane
	Re-costed	(2.64,2.40)	100% isobutylene
Scenario 5	Market-based	(1.03,0.91)	28% naphtha
	Re-costed	(3.99,1.63) (3.03,1.24)	26% naphtha

Table 8. The maximum percentage of defossilization under the defined scenarios based on market-based and re-costed economic parameters.

from the Port of Rotterdam are defined to assess the transition using the proposed optimization model. The results demonstrate: (i) a reduction in the RoI of potential portfolios when ACS-based plants are integrated, highlighting the need for government subsidies to support investment; (ii) furthermore, by applying an allocation method where the prices of ACS-based (by-)products are re-costed, the transition becomes somewhat more attractive, enabling a certain extent of defossilization for decision-makers; (iii) however, it is observed that full defossilization is not achieved based on either market-based or re-costed prices, which highlights the critical role of governmental support in making the transition towards ACS-based technologies more competitive. While this work focuses on economic feasibility, future research can extend this by incorporating environmental and technical perspectives into the optimization model through appropriate constraints or penalties. Additionally, utilizing stochastic optimization methods, which reduce reliance on massive historical data and provide deeper insights into uncertainties such as the quality and quantity of materials and utilities, represents another direction for future investment analysis.

Data availability
The datasets generated and analyzed during the current study are available in supplementary materials A.

Received: 29 September 2025; Accepted: 1 January 2026
Published online: 26 January 2026

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Acknowledgements
The authors would like to thank Michael Tan, Tonny Manalal, and Inna Stepchuk for the bottom-up model development.

Author contributions
A.M.: Conceptualization, Methodology, Data collection, Software, Formal analysis, Writing - original draft, Writing - review & editing. A.R.R: Conceptualization, Supervision, Writing - review & editing, Funding acquisition, Project administration.

Funding
This work has received the financial support of the project 'Unravelling the Impacts of Using Alternative Raw Materials in Industrial Clusters,' project number VI.C.183.010, part of the VICI research programme funded by the Dutch Research Council (NWO).

Declarations

Competing interests
The authors declare no competing interests.

Additional information
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