Integrating superstructure-based design of molecules, processes, and flowsheets

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Abstract
The key to many chemical and energy conversion processes is the choice of the right molecule, for example, used as working fluid. However, the choice of the molecule is inherently coupled to the choice of the right process flowsheet. In this work, we integrate superstructure-based flowsheet design into the design of processes and molecules. The thermodynamic properties of the molecule are modeled by the PC-SAFT equation of state. Computer-aided molecular design enables considering the molecular structure as degree of freedom in the process optimization. To consider the process flowsheet as additional degree of freedom, a superstructure of the process is used. The method results in the optimal molecule, process, and flowsheet. We demonstrate the method for the design of an organic Rankine cycle considering flowsheet options for regeneration, reheating, and turbine bleeding. The presented method provides a user-friendly tool to solve the integrated design problem of processes, molecules, and process flowsheets.

KEYWORDS
CAMD, integrated molecule and process design, organic Rankine cycle, PC-SAFT, superstructure optimization

1 | INTRODUCTION

To maximize the thermo-economic benefit of processes in energy and chemical engineering, the processes have to be tailored to their specific application. Besides the optimization of the process settings, the design of processes usually offers two further degrees of freedom: First, the selection of the right molecule used as processing material, for example, as working fluid or solvent, and second, the selection of the right flowsheet configuration of the process. The most efficient processes thus require the optimal combination of process settings, molecule, and flowsheet configuration. The problem of the selection of process, molecule, and process flowsheet occurs, for example, for separation, reaction, or heat transformation processes. In this work, we exemplify the design of processes, molecules, and process flowsheets for the design of a heat transformation process, the organic Rankine cycle (ORC). ORCs transform low- and medium-temperature heat into electrical power. Thus, the following literature review is mainly focused on the selection of working fluids and flowsheet configurations for ORCs, but we emphasize that important literature is also available for chemical processes (see, e.g., the reviews of Chen and Grossmann or Tian et al).

To select the right molecule, heuristic guidelines and experience are commonly used to identify a list of potential candidate molecules. Subsequently, potential flowsheet configurations are defined and each candidate molecule is assessed by process optimization for each preselected flowsheet configuration. However, the separation of molecule selection, flowsheet selection, and process optimization may lead to suboptimal solutions if the preselection of the molecules or flowsheet configurations fails.
To capture all trade-offs between the molecules and processes, methods developed recently aim at directly integrating the molecule selection into process optimization. Such integrated design methods are commonly based on computer-aided molecular design (CAMD) formulations to capture the vast molecular design space. CAMD formulations allow for the in silico design of molecular structures based on discrete functional groups. The discrete molecular structure makes the integrated design problem a challenging mixed-integer nonlinear programming (MINLP) problem. However, an enumerative assessment of flowsheet configurations is often time-consuming. Methods for the integrated design based on CAMD have been developed, for example, for the design of working fluids for ORCs, refrigerants for heat pumps, mixtures, solvents for absorption processes, extraction processes, or reactions. Methods for the integrated design of processes and molecules usually consider a fixed predefined process flowsheet configuration. However, the choice of the right flowsheet is crucial to maximize the thermodynamic and thermo-economic performance of the processes.

To consider the influence of the process flowsheet, methods for the integrated design of molecules and processes have been extended by an enumerative assessment of preselected flowsheet configurations. Palma-Flores et al. presented a two-stage approach for the design of ORCs. In the first stage, a set of pure working fluid candidates is obtained from CAMD using multiobjective optimization based on pure component properties. The working fluid candidates are subsequently assessed in individual process optimizations for three ORC process flowsheets with optional regeneration and turbine bleeding. Scheffczyk et al. integrated the selection of optimal flowsheet configurations into their framework for the integrated solvent and process design. Computationally efficient pinch-based process models enable an enumerative assessment of four flowsheet configurations directly within the integrated design. However, an enumerative assessment of flowsheet configurations is often time-consuming and limits the integrated design to a small set of preselected flowsheet configurations which might be suboptimal.

To avoid limiting the search space to preselected flowsheet configurations, decomposition-based flowsheet design methods have been developed, integrating the selection of the flowsheet configuration as a degree of freedom to process optimization. Yu et al. proposed a two-stage method to integrate ORCs into heat exchanger networks considering a superstructure of the ORC flowsheet with optional regeneration and turbine bleeding. The working fluid for the ORC is selected from three preselected working fluids, which are enumerated optimally. Elsido et al. presented a superstructure-based method for thermo-economic optimization of ORCs and heat exchanger networks. The superstructure of the ORC includes regeneration, reheating, and multi-pressure level steam cycles. An enumerative optimization of four preselected working fluids is performed to select the optimal working fluid for the ORC. The superstructure-based design of ORCs and heat exchanger networks has been linked to an initial screening approach by Castelli et al. In the initial screening, three promising working fluids are first selected from a set of over 100 pure components and mixtures based on an ideal cycle. Lee et al. optimized an ORC superstructure for a single pre-defined ternary working fluid mixture to utilize cryogenic exergy from liquid natural gas. A genetic algorithm (GA) is used to identify the optimal process configuration and process conditions considering 1,024 possible process alternatives.

GAs have also been used to efficiently select molecules from a set of preselected candidates in order to prevent an enumerative assessment of molecules within superstructure-based process design. Stijepovic et al. present a framework for the design of cascade ORCs, which identifies the optimal number of cascades as well as the process conditions and working fluid of each cascade. The working fluids are selected by a GA from a pre-defined set of seven working fluids. Bao et al. used a GA to simultaneously select the optimal flowsheet from 9 configurations and the optimal working fluid from 12 molecules for 3-stage condensation Rankine cycles. A two-stage approach for the integration of ORCs for waste heat recovery in industrial processes has been presented by Kermani et al. In the first stage, the process conditions are optimized and the working fluid is selected from 14 working fluid candidates by a GA. Subsequently, the resulting mixed-integer linear programming (MILP) optimization problem of ORC superstructure and equipment sizes is solved. The superstructure of the ORC involves regeneration, reheating, turbine bleeding as well as transcritical and multi-stage cycles. However, the superstructure-based flowsheet design has still been performed for a small set of fixed preselected molecules.

To extend both, the design space of the molecules and of the flowsheets, decomposition methods have been developed, which link CAMD to superstructure-based design of flowsheet configurations. In a first stage of such decomposition methods, the design space of the molecules and/or flowsheets is reduced, for example, using CAMD with heuristic constraints based on guidelines and experience or multi-objective optimization with molecular cluster techniques. In a second stage, the resulting MINLP is solved or individual process optimizations are performed if the number of remaining feasible solutions is small. In the second stage, the considered process models can consist of a detailed superstructure including discrete process flowsheet decision variables to select the flowsheet configuration. Decomposition procedures rely on the assumption that the molecules and/or process flowsheets, which are initially identified based on heuristic constraints or multi-objective optimization, will also be overall beneficial in the final process optimization. If the first stage does not capture all inherent trade-offs between process, molecule, and flowsheet, the solutions are suboptimal.

To obtain overall optimal solutions, CAMD formulations have been directly integrated into the flowsheet design. In pioneering work, Linke and Kokossis simultaneously designed reaction-separation processes and solvents combining CAMD with a superstructure of generic synthesis units. The problem is solved using stochastic optimization by simulated annealing. The work shows the benefit and importance of an integrated design of process, molecule, and flowsheet configuration. Gopinath extended her earlier work for the integrated design of solvents based on physical domain reduction by process.
synthesis. For this purpose, structural decision variables of the process have been included in the integrated design framework using a modified state operator network. The equilibrium properties of the molecule are calculated using the SAFT-$\gamma$ Mie equation of state (EoS), while transport properties are calculated using standard group contribution (GC) methods. The framework is implemented in C++ with an interface to the commercial simulator gPROMS ModelBuilder to solve the subproblems and an interface to Gurobi to solve the master problem of the resulting MINLP problem. The method has been exemplified for liquid-liquid-extraction of butanol from water, where two binaries control the selection of optional heat exchangers. The works of Linke and Kokossis and Gopinath highlight the advantages of integrating molecule and flowsheet design. However, such an integrated design of process, molecule, and flowsheet configuration is still rarely investigated in literature. Current integrated design methods still lack a consistent thermodynamic model with strong predictive power for both equilibrium and transport properties. Furthermore, a generic solution method solely based on a standard engineering tool is still missing, which would allow for an easy application of the whole integrated design.

In this work, we present a generic solution method for the integrated thermo-economic design of processes, molecules and flowsheets based on a consistent thermodynamic model for equilibrium as well as transport properties and a process flowsheeting software. With this method, the right molecules and flowsheet configurations are efficiently selected in a single MINLP optimization problem considering a large molecular design space and a superstructure-based design of the flowsheet configuration. The presented work is based on our previously presented 1-stage continuous-molecular targeting – computer-aided molecular design (1-stage CoMT-CAMD) framework for the integrated design of molecules and processes. Within 1-stage CoMT-CAMD, a CAMD formulation is directly linked to a detailed model of the process. The physically based PC-SAFT EoS is used to model the thermodynamic properties of the molecules. The integration of transport properties calculated based on entropy-scaling and PC-SAFT enables a detailed sizing of the equipment and thus a thermo-economic objective. The resulting 1-stage CoMT-CAMD method can be applied to steady-state processes or transient processes.

Prior to this work, 1-stage CoMT-CAMD was limited to an initially defined fixed flowsheet configuration. In this work, a superstructure of the process model is directly integrated into 1-stage CoMT-CAMD enabling the selection of the flowsheet configuration as a degree of freedom of the MINLP optimization problem. The CAMD formulation ensures consideration of a large molecular design space, while the process superstructure enables a systematic and efficient selection of the optimal flowsheet configuration. The process flowsheeting software gPROMS ProcessBuilder is used to model the process superstructure allowing for easy development and adaption of the process superstructure based on existing model libraries. The PC-SAFT EoS is used as a thermodynamically consistent model to model both, equilibrium and transport properties. Detailed models for equipment sizing allow a thermo-economic design of the molecules, processes, equipment, and flowsheet configurations. The whole framework is implemented in gPROMS ProcessBuilder, which is used as standard engineering tool to solve the integrated design problem.

The integrated design is exemplified for the design of an ORC. The superstructure of the ORC includes optional units for regeneration, turbine bleeding, and reheating. The presented method enables us to identify the optimal working fluid and corresponding optimal process, equipment sizes and flowsheet configuration in a single MINLP optimization problem.

The paper is structured as follows: in Section 2, the 1-stage CoMT-CAMD method for the integrated design of molecules, processes, equipment, and flowsheet configurations is described. The case study for the design of an ORC used to exemplify the presented method is introduced in Section 3. The results of the integrated design are presented and discussed in Section 4 and conclusions are drawn in Section 5.

## 2 | FRAMEWORK FOR INTEGRATED DESIGN OF MOLECULES, PROCESSES, EQUIPMENT AND FLOWSHEET

The presented 1-stage CoMT-CAMD method aims at optimizing the thermodynamic and economic performance of processes by exploiting the design space of the molecules as well as the flowsheet configurations. For the design of the molecular structure, a CAMD formulation is used, while the design of the flowsheet configuration is enabled by a superstructure of the process model. The design of both, molecule and flowsheet configuration, is directly coupled to the process design itself. The thermo-economic design of molecules, processes, equipment, and flowsheet configurations can be decomposed into eight levels (see Figure 1), one target level, four design levels, and three connector levels: on level 1, the target level, the assessment criterion of the optimization is defined as the economics of the process calculated based on operating and investment cost. For this purpose, a process flowsheet is needed to define the process units and their connectivity. The flowsheet configuration is designed (level 2: design) using a superstructure model (level 3: connector). The superstructure model contains all possible flowsheet configurations. To determine the operating and investment cost for the flowsheet configuration, equipment sizes and process settings are required. The equipment is designed using detailed models for equipment sizing (level 4: design) based on transport properties of the molecule (level 5: connector). Process settings are calculated from a thermodynamic process model that determines all states of the process (level 6: design). For this purpose, thermodynamic equilibrium properties of the molecule are needed (level 7: connector). In this work, both equilibrium and transport properties are calculated using the thermodynamically consistent PC-SAFT EoS. The molecular structure is finally designed based on a CAMD formulation (level 8: design). Due to the strong interaction of all eight levels, the integrated design is simultaneously performed in a single optimization problem for all levels.
2.1 Problem definition

A general problem formulation of the MINLP optimization problem for the integrated design of process and molecule has been presented by Gani. In this work, the MINLP includes the design of the flowsheet configuration and can be formulated as:

\[
\min_{x, \theta, \kappa, w} f(x, \theta, \kappa, w)
\]

s.t. \( S_1 w + S_2(x, \theta, \kappa) \leq 0 \) \( \{ \) superstructure model \( \}

\( g_1(x, \theta, \kappa) = 0 \)

\( g_2(x, \theta, \kappa) \leq 0 \)

\( \kappa = k(x, \theta, y^S) \) \( \{ \) PC-SAFT (transport) \( \}

\( p_1(x, \theta) = 0 \)

\( p_2(x, \theta) \leq 0 \)

\( \theta = h(x, y^S) \) \( \{ \) PC-SAFT (equilibrium) \( \}

\( F_1 \cdot y^S = 0 \)

\( F_2 \cdot y^S \leq 0 \)

\( x_0 \leq x \leq x_0 \in \mathbb{R}^n \) \( \{ \) process degrees of freedom \( \}

\( y^S_0 \leq y^S \leq y^S_0 \in \mathbb{R}^m \) \( \{ \) molecular structure \( \}

\( w \in (0, 1]^l \) \( \{ \) structural decision variables \( \)

\( \{ \) nonlinear functions using the matrix \( S_1 \). The process and equipment models are composed of equality constraints \( (g_1, p_1) \) (e.g., energy balances) and inequality constraints \( (g_2, p_2) \) (e.g., pressure limits). Both, equilibrium properties \( \theta \) and transport properties \( \kappa \) of the molecule are calculated from the molecular structure \( y^S \) using the PC-SAFT EoS as thermodynamic model (see Section 2.3). The vector \( y^S \) contains the number of functional groups constituting the molecular structure of the molecule. The CAMD formulation allows the design of novel molecular structures \( y^S \) as a degree of freedom of the optimization problem. Structural feasibility is ensured by additional equality and inequality CAMD constraints \( (F_1, F_2, \text{e.g., octet rule}) \).

The degrees of freedom of the resulting MINLP are the continuous process and equipment variables \( x \), the molecular structure \( y^S \) of the molecule and the structural decision variables \( w \) representing the flowsheet configuration. Solving the MINLP given in Problem (1) yields the integrated thermo-economic design of molecules, processes, equipment, and flowsheet configurations. The result of the optimization problem is the optimal structure of the molecule and the corresponding optimal process, equipment, and flowsheet configuration. To allow for an a posteriori assessment of the identified solution, a ranking of optimal molecules and flowsheet configurations can be obtained using integer-cut constraints (see Section 2.4). A ranking list of optimal molecules is useful to account for molecule-constraints, such as corrosion behavior, that rely on expert experience and where no suitable mathematical model is available.

2.2 Superstructure modeling

To consider the flowsheet configuration as a degree of freedom during optimization, a superstructure of the considered process is used which includes all possible flowsheet configurations with their corresponding unit models. The additional unit models introduce optional process degrees of freedom, equality, and inequality constraints, such as corrosion behavior, that rely on expert experience and where no suitable mathematical model is available.
constraints. The selection of a unit can often be controlled by the corresponding continuous process variables. For example, a heat flow \( \dot{Q} \) greater than zero indicates the selection of an optional heat exchanger. However, the selection of a unit usually affects additional constraints of the unit, which have to be activated if a unit is selected and vice versa. For this purpose, binary structural decision variables \( w \) are introduced to control the flowsheet configuration by

\[
w_i = \begin{cases} 
1 & \text{if unit } i \text{ is selected in the optimal flowsheet configuration,} \\
0 & \text{otherwise.}
\end{cases}
\]

On the one hand, the binary structural decision variables \( w \) are used to link unit models and process variables. On the other hand, the variables \( w \) enable us to activate and deactivate constraints or fixed terms of equations.\(^{40}\) The process variables \( x_i \) (e.g., heat flows or temperature differences) are linked to binary structural decision variables \( w_i \) in additional inequality constraints \( S_i^1 \cdot w + S_i^2(x, \theta, \lambda) \leq 0 \) in Problem (1)\(^{40,64}\).

\[
x_i \leq (1-w_i)U_0 + U_1w_i,
\]

\[
x_i \geq (1-w_i)L_0 + L_1w_i,
\]

where \( U_1 \) as well as \( U_0 \) are upper bounds and \( L_2 \) as well as \( L_0 \) are lower bounds of the variable \( x_i \). The bounds \( U_1 \) and \( L_2 \) of the process variable \( x_i \) are active if the corresponding unit is selected in the optimal flowsheet configuration (e.g., minimal areas for optional heat exchangers). In contrast, the bounds \( U_0 \) and \( L_0 \) of the process variable \( x_i \) are active if the corresponding unit is not included in the optimal flowsheet configuration. The upper and lower bounds can be used to fix variables (e.g., \( L_0 = U_0 = 0 \) as bounds of the heat flow if a heat exchanger is not selected) or to relax constraints using big-M constraints (e.g., if a heat exchanger is not selected, the limit on the minimal temperature differences is relaxed to a large negative number \( L_0 \ll 0 \)).

The nonlinear models of the process often contain functions \( \Phi(p(x)) \), which are only defined for \( p(x) \geq 0 \) or \( p(x) > 0 \), for example, logarithms. However, singularities of \( p(x) \) can occur if a unit is not included in the flowsheet configuration or a poor initial guess is chosen leading to infeasible solutions and unstable performance of the optimization problem. To stabilize the convergence, we use an approximation \( \tilde{p}(x) \) of \( p(x) \), which ensures a positive, continuous and differentiable function for \( p(x) \leq \epsilon \):

\[
\tilde{p}(x) = \begin{cases} 
\frac{p(x)}{\epsilon} & \text{if } p(x) \geq \epsilon \\
\frac{\epsilon}{\epsilon + e^{p(x)}/}\epsilon & \text{if } p(x) < \epsilon
\end{cases}
\]

where \( \epsilon \) is a small positive tolerance.\(^{64}\) The function \( \tilde{p}(x) \) is positive and continuous as well as differentiable at the threshold \( p(x) = \epsilon \) ensuring a more stable convergence of the optimization problem. The approximation \( \tilde{p}(x) \) is used in this work for functions \( p(x) \) occurring in logarithms or roots.\(^{64}\)

## 2.3 CAMD using group-contribution PC-SAFT

The equilibrium as well as transport properties of the molecule are calculated in a thermodynamically consistent way using the PC-SAFT EoS.\(^{57}\) In PC-SAFT, a molecule is represented by perturbed chains of spherical segments. The perturbed chains are typically described by three to seven physically based pure component parameters \( z \). In this work, we consider only nonpolar and nonassociative molecules. Thus, three pure component parameters are sufficient to represent a molecule: the segment diameter \( \sigma \) and the segment number \( m \) characterize the geometry of the chains and the segment dispersion energy \( \epsilon/k \) describes the van der Waals attraction. Due to their physical basis, the pure component parameters show good relation to the molecular structure making the parameters suitable for optimization by relaxation strategies\(^{16,27,65}\) and GC methods.\(^{17,66}\) The strong predictive power of the PC-SAFT EoS to calculate equilibrium and transport properties allows for a clear distinction of the identified molecules if the molecular structures are not too similar, for example, propene and propane, as demonstrated in an uncertainty analysis by Schilling et al.\(^{18}\)

PC-SAFT is linked to the CAMD formulation using the homosegmented GC method of PC-SAFT.\(^{66}\) Thereby, the pure component parameters \( z \) are calculated from the molecular structure \( y^5 \) of the molecule. The GCs of the pure component parameters have been adjusted to measurement data of a database for vapor–liquid equilibrium and liquid densities.\(^{66}\) The pure component parameters are calculated from the molecular structure using the mixing rules of Vijande et al.\(^{67}\):

\[
\begin{align*}
z_1 &= m = \sum_{k \in K} n_k m_k, \\
z_2 &= m \sigma^2 = \sum_{k \in K} n_k m_k \sigma_k^2, \\
z_3 &= m \epsilon/k = \sum_{k \in K} n_k m_k (\epsilon/k)_k,
\end{align*}
\]

where \( n_k \) denotes the number of functional groups of type \( k \) contained in the molecular structure. The molecular structure is represented by the vector \( y^5 = (n_1, n_2, ..., n_5)^T \) with the GCs of group \( k \) \( z = (m_k, \sigma_k, (\epsilon/k)_k)^T \). The uncertainties of the considered group-contribution method of PC-SAFT lead to an expected average error in a thermodynamic objective of less than 1%.\(^{57}\) Property uncertainties of the thermodynamic model can be taken into account within the integrated design method, for example, using sensitivity analysis\(^{26}\) or Monte Carlo based optimization strategies.\(^{19}\)

PC-SAFT provides a consistent thermodynamic model for the computation of both, equilibrium and transport properties based on the residual Helmholtz energy. To calculate absolute properties from the residual properties, a reference property is needed. In this work, the heat capacity of ideal gas \( c_v^0 \) is used as reference property calculated from the molecular structure \( y^5 \) using Joback’s GC method.\(^{68}\) Thereby, absolute caloric properties, for example, the absolute enthalpy difference \( h \), can be calculated as the sum of a residual...
contribution (res) and an ideal contribution (id) for a given pressure \( p \) and temperature \( T \) from:

\[
h(p, T, y^s) = h^{\text{res}}(p, T, z(y^s)) + h^{\text{id}}(T, y^s)
= h^{\text{res}}(p, T, z(y^s)) + \int_{T_0}^T \alpha^{\text{sh}}(T, y^s) \, dT,
\]

where \( T_0 \) is an arbitrary reference temperature.

The calculation of the transport properties \( \kappa \) from PC-SAFT has been proposed by Lötgering-Lin and Gross\(^{58}\) for viscosities \( \eta \) and by Hop and Gross\(^{69}\) for thermal-conductivities \( \lambda \). The models are based on Rosenfeld’s entropy scaling\(^{70,71}\), who proposed that transport properties are an univariate function of the residual entropy \( s_{\text{res}} \). The univariate functions have been determined for many different molecules. Furthermore, GC methods have been proposed to calculate transport properties\(^{58,59}\). The viscosity and the thermal conductivity are important transport properties for heat transformation processes, for example, ORCs. For processes from chemical engineering, also diffusion coefficients are important to describe the mass transfer. The group around Gross has also developed models for the prediction of self-diffusion coefficients based on entropy scaling and PC-SAFT\(^{72}\) which could thus also be easily implemented into the presented 1-stage CoMT-CAMD method.

In this work, GC methods are used for the calculation of the pure component parameters \( z \), the heat capacity of the ideal gas \( c_p^\text{id} \), the adjustable parameters in the univariate functions for the transport properties and for the molar mass \( M \). The functional groups are limited to the range of measurement data that was available to adjust the GCs. To prevent extrapolation from the molecular families considered in the database, we consider additional inequality constraints \( F_{\text{z}} \cdot \gamma^z \leq 0 \) in Problem (1) to limit the molecular design space. The functional groups considered in this work are: \(-\text{CH}_2\), \(-\text{CH}_3\), \(-\text{CH}=\), \(-\text{C}+=\) for branched alkanes, \(-\text{CH}_2=\text{CH}\), \(-\text{CH}==\) and \(-\text{C}=\) for branched alkenes, \(-\text{CH}_2\text{C}=\text{CH}\), \(-\text{CH}=\text{CH}\), \(-\text{CH}_2\text{CH}=\text{CH}\), \(-\text{CH}=\text{CH}_2\), \(-\text{CH}_2\text{CH}==\text{CH}\) and \(-\text{CH}_2\text{C}=\text{CH}_2\) for cyclic components with alkyl side groups. The number of groups is currently mainly limited by the available data for transport properties and the lack for the polar contribution of the PC-SAFT EoS\(^{73,74}\) in gPROMS ProcessBuilder. Therefore, the considered molecular design space is comparatively small. However, additional groups can be easily integrated into the method as soon as the GC approaches are further developed or polar contributions of PC-SAFT are considered.

2.4 Optimization strategy and implementation

1-stage CoMT-CAMD allows both single- and multi-objective optimization\(^{17,19}\). The result of a single-objective optimization is a single optimal molecule and the corresponding optimal process, equipment and flowsheet configuration. A ranking of optimal solutions can be calculated using integer-cut constraints\(^{63}\). Here, the MINLP is solved repeatedly and additional integer-cut constraints exclude previous solutions from the design space, that is, previously identified molecules and/or flowsheet configurations. The result of a multi-objective optimization is a Pareto front calculated, for example, by the normal constraint method\(^{75}\).

To make the method more user friendly, 1-stage CoMT-CAMD has been implemented in the flowsheeting software gPROMS ProcessBuilder 1.2 developed by Process System Enterprise Ltd.\(^{55}\). The gPROMS ProcessBuilder is a process modeling software for process simulation and optimization including equipment model libraries for processes from energy and chemical engineering. The equipment model libraries allow for an easy drag-and-drop flowsheeting of the process. The implementation of 1-stage CoMT-CAMD into gPROMS ProcessBuilder provides a user-friendly design tool that engineers can use on a daily basis overcoming the challenge of previous integrated design approaches, which are based on specific tools\(^{76}\). In our previous work, we have integrated 1-stage CoMT-CAMD into gPROMS ProcessBuilder for an integrated thermodynamic design of processes and molecules.\(^{77}\) The thermodynamic properties are calculated using the PC-SAFT EoS available in the gSAFT property package of gPROMS ProcessBuilder. The CAMD formulation has been implemented directly in the gPROMS ProcessBuilder to consider the molecular structure as a degree of freedom of the process optimization using the variable molecular structure compounds feature. In this work, the implementation of 1-stage CoMT-CAMD in gPROMS ProcessBuilder has been extended by models for the calculation of transport properties based on PC-SAFT (see Section 2.3), models for sizing of the equipment allowing through costing functions the optimization of a thermo-economic objective\(^{18}\) and models for a superstructure-based flowsheet optimization. With these features, the integrated design problem is easily defined using the drag- & drop feature of the gPROMS ProcessBuilder. The process superstructure can be defined using the equipment model libraries of gPROMS ProcessBuilder. While the use of the model library is convenient, it comes at the disadvantage that the models are usually encrypted for the user. To solve larger optimization problems, an efficient treatment of the underlying mathematical problem is often needed which usually requires knowledge of the model equations. If such more advanced superstructure solution methods are used (see, e.g., Yeomans and Grossmann\(^{79}\)), the gPROMS custom modeling package can be used to implement user-specific equipment models. The resulting MINLP optimization problem given in Problem (1) is solved using the standard MINLP solver of gPROMS ProcessBuilder: OaERAP (outer approximation/equality relaxation/augmented penalty). The OAERAP solver combines an outer approximation formulation with a relaxation strategy. The relaxation corresponds to the CoMT problem in 1-stage CoMT-CAMD. The initially solved relaxed problem leads to a hypothetical optimal molecular structure, the target, and a hypothetical optimal flowsheet configuration serving as a lower bound of the optimization problem. Subsequently, loops of MILP master problems and NLP subproblems are solved to identify the optimal real molecular structure as well as real flowsheet configuration jointly with the corresponding optimal process and equipment. Alternatively, to use more advanced MINLP solvers, an optimization framework can be built around gPROMS ProcessBuilder, as for example, presented by Gopinath.\(^{54}\).
3 | CASE STUDY: ORGANIC RANKINE CYCLE

The integrated design of molecules, processes, equipment, and flowsheet configurations is applied for the design of a subcritical ORC for waste heat recovery. The basic ORC process comprises four main steps: in step 1, the pressure level of the liquid working fluid is increased in a pump. In step 2, the working fluid is preheated, evaporated, and optionally superheated in a preheater and evaporator utilizing a low- or medium-temperature heat source. In step 3, the working fluid is expanded to the lower pressure level in a turbine. The mechanical work of the turbine is transformed into electrical power by a generator. In step 4, the working fluid is desuperheated and condensed in the condenser to close the cycle. Beyond the basic ORC, possible ORC flowsheet configurations include regeneration with a regenerator or by turbine bleeding, reheating, vapor injectors, transcritical cycles, trilateral cycles, multi-stage cycles, or cascade cycles. To demonstrate the integrated design of the flowsheet configuration, we extend the basic cycle in the superstructure by three flowsheet options and their combinations discussed in the recent literature: (a) regeneration, (b) turbine bleeding, and (c) reheating (Figure 2):

a. **Regeneration**: heat at the outlet of the turbine is recovered to pre-heat the working fluid after pumping. Thereby, exergy losses are reduced but an additional heat exchanger is required.

b. **Turbine bleeding**: part of the steam is extracted from the turbine at an intermediate pressure level to heat the working fluid condensate, which in turn reduces exergy losses. Here, we consider direct heating by non-isothermal mixing of the condensate and the extracted steam. Thereby, an additional heat exchanger is avoided. However, an additional pump and a multi-stage expander are required to extract the steam and turbine work is lost.

c. **Reheating**: the working fluid is reheated at an intermediate pressure level before further expansion. Thereby, heat recovery is increased and the temperature after the second turbine is raised to improve the regeneration. However, an additional heat exchanger and an additional turbine are required.

All flowsheet options increase the mean temperature difference between heat input and heat rejection and thus increase thermal efficiency. However, additional equipment is required leading to higher total capital investment. Thus, the flowsheet configuration has to be considered as degree of freedom within the integrated design to evaluate the trade-off between higher thermal efficiency and higher total capital investment. The implementation of the ORC superstructure in gPROMS ProcessBuilder is illustrated in Figure 3 showing also the newly developed models for CAMD and sizing of the heat exchangers. Since flowsheet options are selected through additional constraints according to Section 2.2, additional splitters/mixers can be avoided (cf. Figure 2). Thereby, a mass flow rate of $\dot{m}_{\text{w}} > 0 \text{ kg/s}$ is ensured in the equipment models, which is required by models of the ProcessBuilder library.

Kermani et al. presented a more generic superstructure for ORCs including regeneration, reheating, turbine bleeding as well as transcritical and multi-stage cycles. Here, we do not consider transcritical cycles due to the poorer quality of equations of state near the critical point. We focus also on a single-stage cycle which is often most economic. However, in general, the presented method is not limited to the given ORC superstructure and can be easily extended in future work by further flowsheet options, for example, multi-stage cycles or cascade cycles.

3.1 | General specifications

In this work, we consider freely available industrial liquid wastewater at $p_{\text{HS}} = 5 \text{ bar}$ as heat source with a mass flow rate of $\dot{m}_{\text{w}} = 15 \text{ kg/s}$, an inlet temperature of $T_{\text{HS}} = 150^\circ \text{C}$ and an outlet temperature of $T_{\text{HS}}^{\text{out}} = 135^\circ \text{C}$ adopted from Chys et al. (Table 1). Cooling water at $p_{\text{CW}} = 4 \text{ bar}$ is assumed as cooling medium in the condenser with an inlet temperature of $T_{\text{CW}} = 15^\circ \text{C}$ and an outlet temperature of $T_{\text{CW}}^{\text{out}} = 30^\circ \text{C}$ taken from Hipólito-Valencia et al. where also the cost for the cooling water $C_{\text{cooling}}$ is provided.

In general, any thermo-economic objective based on operating cost and investment cost can be considered in the optimization.
problem. In this work, we consider the net present value NPV as objective calculated as:

\[
f(x, \theta, \kappa, w) = \text{NPV} = (\text{RE} - \text{TOC}) \cdot PVAF - TCI
\]

with

\[
\text{RE} = \frac{P_{\text{net}} \cdot \tau \cdot e_{\text{el}}}{\eta_{\text{is}}},
\]

\[
\text{TOC} = C_{\text{cooling}} + C_m = \dot{Q}_{\text{cooling}} \cdot \tau \cdot C_{\text{cooling}} + \frac{\dot{m}_{\text{net}}}{\eta_{\text{is}}} \cdot TCI.
\]

Here, the annual revenue from electricity sales \( \text{RE} \) is calculated from the net power output \( P_{\text{net}} \), the annual operating hours \( \tau \) and the selling price for electricity \( e_{\text{el}} \) (Table 1). The total annual operating cost \( \text{TOC} \) includes cost for cooling and maintenance. The cooling cost \( C_{\text{cooling}} \) is calculated from the heat flow in the condenser \( Q_{\text{condenser}} \) as well as the cost for cooling water \( C_{\text{cooling}} \) and the annual maintenance cost \( C_m \) is estimated as a share \( \frac{\dot{m}_{\text{net}}}{\eta_{\text{is}}} \) of the total capital investment \( \text{TCI} \). The present value annuity factor \( PVAF \) is calculated from the lifetime \( n = 25a \) and the rate of return \( i = 0.08 \). The total capital investment \( \text{TCI} \) is calculated as sum of the purchased-equipment cost \( \text{PEC}_{\text{RE},m} \) multiplied by factors for additional direct and indirect costs \( S^{22,33} \) (for details see Schilling et al\(^{19b}\)):

\[
\text{TCI} = 3.7 \cdot \sum_{m = M} \text{PEC}_{\text{RE},m} + 3.1 \cdot \sum_{n = N} \text{PEC}_{\text{HE},n}.
\]

where \( \text{PEC}_{\text{RE},m} \) denotes the purchased-equipment cost of the rotating equipment \( m \) and \( \text{PEC}_{\text{HE},n} \) indicates the purchased equipment cost of the heat exchanger \( n \) (see Section 3.2). The net power output \( P_{\text{net}} \) is calculated as:

\[
P_{\text{net}} = \sum_{j = J} P_{\text{T},j} - \sum_{k = K} P_{\text{P},k},
\]

where \( P_{\text{T},j} \) denotes the power output of the turbine \( j \) and \( P_{\text{P},k} \) indicates the power input of the pump \( k \).

The continuous degrees of freedom of the basic ORC \( x = (m_{\text{net}}, p_{\text{cond}}, p_{\text{evap}}, \Delta T_{\text{reheating}}, \Delta T_{\text{turbine bleeding}}) \) are the mass flow rate of the working fluid \( m_{\text{net}} \), the pressure levels in the condenser \( p_{\text{cond}} \) as well as the evaporator \( p_{\text{evap}} \) and the degree of superheating after evaporation \( \Delta T_{\text{reheating}} \) and turbine bleeding \( \Delta T_{\text{turbine bleeding}} \). To select the flowsheet configuration, three binary structural decision variables \( w \) are used for regeneration, turbine bleeding, and reheating. The optional flowsheet configurations introduce five additional degrees of freedom \( x_{\text{op}} = (\dot{Q}_{\text{cond}}, \dot{Q}_{\text{turbine bleeding}}, \dot{Q}_{\text{reheating}}, \dot{Q}_{\text{reheating}}, \dot{Q}_{\text{reheating}}) \) which are the heat flow for regeneration \( \dot{Q}_{\text{reg}} \), the mass split fraction for turbine bleeding \( \zeta_{\text{turbine bleeding}} \), the pressure ratio for turbine bleeding \( \psi_{\text{turbine bleeding}} \), the pressure ratio of the turbine for reheating \( \psi_{\text{reheating}} \) and the heat flow for reheating \( \dot{Q}_{\text{reheating}} \). In summary, three binary structural decision variables and nine continuous process degrees of freedom \( x = x_{\text{c}} \cup x_{\text{op}} \) are

| Parameter | Symbol | Value |
|-----------|--------|-------|
| Flow rate (heat source) | \( m_{\text{HS}} \) | 15 kg/s |
| Inlet temperature (heat source) | \( T_{\text{HS}} \) | 150°C |
| Outlet temperature (heat source) | \( T_{\text{out, HS}} \) | 135°C |
| Inlet temperature (cooling water) | \( T_{\text{CW}} \) | 15°C |
| Temperature rise (cooling water) | \( \Delta T_{\text{CW}} \) | 15 K |
| Annual operating hours | \( \tau \) | 8.000 h/a |
| Selling price for electricity | \( e_{\text{el}} \) | 61.6€/MWh |
| Costs for cooling water | \( C_{\text{cooling}} \) | 1.12€/MWh |
| Share for annual maintenance cost | \( i_{\text{OC}} \) | 0.02a⁻¹ |
| Lifetime | \( n \) | 25a |
| Rate of interest | \( i \) | 0.08 |
| Exchange rate | \( c_{\text{€-\$}} \) | 1.136 €/$ |
| Min. steam quality (turbine outlets) | \( \phi_{\text{min}} \) | 1 |
| Isentropic turbine efficiency | \( \eta_{\text{is}} \) | 0.8 |
| Isentropic pump efficiency | \( \eta_{\text{pump}} \) | 0.65 |
| Mechanical efficiency (turbines/pumps) | \( \eta_m \) | 0.97 |
| Minimal absolute pressure | \( p_{\text{min}} \) | 1 bar |
| Maximal absolute pressure | \( p_{\text{max}} \) | 50 bar |
| Maximal reduced pressure | \( p_{\text{red}} \) | 0.85 |
| Maximal segment number | \( n_{\text{max}} \) | 25 |

FIGURE 3  ORC superstructure including regeneration, turbine bleeding, and reheating. The flowsheet is created using gPROMS ProcessBuilder 1.2.55 An overview of all models used for the flowsheet is given in the Supporting Information, Section S1 [Color figure can be viewed at wileyonlinelibrary.com]
considered in the optimization problem. The continuous process degrees of freedom of the optional flowsheet configurations are only active if the corresponding unit is selected in the flowsheet configuration. Otherwise, the continuous degrees of freedom \( x_{op} \) are set to 0 for the heat flows as well as the split fraction \( (L_0 = U_0 = 0) \) and to 1 for the pressure ratios \( (L_0 = U_0 = 1) \) using Equations (3) and (4):

\[
L_1 \cdot w_i \leq \bar{x}_i \leq U_1 \cdot w_i \\
(1-w_i) + L_1 \cdot w_i \leq \bar{x}_i \leq (1-w_i) + U_1 \cdot w_i
\]

for \( \bar{x}_i \in \{ Q_{\text{reg}, i}, \bar{\dot{Q}}_{\text{reh}} \} \) \hspace{1cm} (13)

If a flowsheet configuration is selected, the constraints ensure that all corresponding units are active (e.g., if reheating is selected, both, the corresponding turbine and heat exchanger have to be active \( [P_{\text{reh}} > 0 \text{ and } A_{\text{reh}} > 0] \)). Finally, the maximal number of functional groups of the molecular structure is limited to \( \sum_{i=1}^{n_k} n_k \leq n_{\text{max}} = 25 \) leading to 5,886 molecular structures fulfilling the constituting CAMD constraints.

### 3.2 Sizing and investment models

The purchased-equipment cost \( PEC_i \) of unit \( i \) is typically calculated as the sum of fixed purchased-equipment cost \( c_f \) and variable purchased-equipment cost in power-law expression:

\[
PEC_i = c_f + c_v \cdot K_i^p
\]

where \( K_i \) denotes the key equipment size or capacity (e.g., heat exchanger area \( A \)), \( c_v \) indicates the cost factor for variable costs and \( \beta_i \) is a unit-specific exponent, often about 0.6–0.7.\(^{64}\) The binary structural decision variables \( w \) are used to deactivate fixed purchased-investment costs of optional units if a unit is not selected. For the calculation of the purchased-equipment cost \( PEC \), we consider the chemical plant index\(^{85}\) to account for inflation and development of raw materials with CEPCI\(_{2016} = 541.7 \) and an exchange rate\(^{86}\) of \( 1,136$/€ \) (details see Schilling et al\(^{18} \)). The purchased-equipment cost \( PEC_{\text{reg}} \) of the rotating equipment (pumps and turbines) are calculated from the power input \( (P_p) \) and output \( (P_t) \) respectively.\(^{57}\) However, the cost correlations given in Turton et al\(^{87}\) are exponential correlations. To obtain an expression according to Equation (20), the factors \( c_{v,T}, c_{v,J} \) and \( \beta_i \) are adjusted to the cost correlations in the relevant interval (details are given in the Supporting information, Section S2). If turbine bleeding is selected, additional purchased-equipment costs have to be considered since a multi-stage turbine is required. As a first guess, we assume a two-stage turbine and estimate the additional cost by calculating the variable contribution \( (c_v \cdot K_j^p) \) individually for each stage leading to slightly higher purchased-equipment cost of the turbine if turbine bleeding is selected. The purchased-equipment cost of the generator is calculated from the net power output \( P_{\text{net}} \).\(^{88}\) The purchased-equipment cost of the heat exchangers \( PEC_{\text{HE}} \) is calculated for carbon steel from the heat exchanger area \( A_{\text{HE}} \).\(^{89}\) The heat exchangers are modeled as shell and tube heat exchangers in counter-flow control without shell baffles. The outer diameter of the tubes is set to \( d_o = 20 \) mm, the inner diameter of the tubes to \( d_i = 16 \) mm and the thermal conductivity of the wall to \( \lambda_{\text{steel}} = 43 \) W m\(^{-1}\) K\(^{-1}\). The number of tubes and shell diameter are calculated considering a maximal allowed velocity in the tubes and the shell, respectively \( (\nu_{\text{max}} = 1.5 \) m/s for liquids and \( \nu_{\text{max}} = 20 \) m/s for vapors). The working fluid is on the tube side and the water for heating and cooling is on the shell side.

The heat-transfer coefficients are calculated outside and inside of the tubes for single phase, evaporation and condensation depending on dimensionless parameters, for example, the Nusselt and Reynolds number. Single phase, forced convection is assumed to calculate the heat-transfer coefficient for the heating water, the cooling water and the working fluid in the preheater, the superheating part of the evaporator, the desuperheating part of the condenser and the heat exchangers for regeneration and reheating\(^{90}\) (Table 2). For
evaporation, a superposition of forced convection and bulk boiling\textsuperscript{91} is assumed with specific correlations for forced convection\textsuperscript{92} and bulk boiling\textsuperscript{93}. For condensation, we use the correlation for filmwise condensation inside horizontal tubes of Shah\textsuperscript{94-96}. The correlations for flow boiling and condensation describe local heat transfer and thus depend on the steam quality (i.e., vapor fraction). Therefore, we discretize the steam quality in 20 intervals and calculate individual heat transfer areas for each interval with constant mean steam quality. Furthermore, the correlation for flow boiling additionally depends on the heat flux density and thus on the heat exchanger area $A_{HE}$ necessitating an iterative calculation of the heat exchanger area.

4 | INTEGRATED DESIGN OF THE ORC

The 1-stage CoMT-CAMD method is used for the integrated design of working fluid, ORC process, equipment, and flowsheet configuration of the case study presented in Section 3. The resulting optimization problem consists of 9 continuous process degrees of freedom $x$, 3 binary degrees of freedom $w$ to describe the flowsheet configuration, and 38 binary degrees of freedom to describe the molecular structure $y$\textsuperscript{2}. A binary notation of the molecular structure is chosen for easy implementation of integer-cuts.\textsuperscript{62} Since only a thermo-economic model is used within 1-stage CoMT-CAMD, the identified molecular structures have to be subsequently assessed regarding further non-thermodynamic properties, for example, toxicity or environmental impacts. These non-thermodynamic properties can be directly integrated into 1-stage CoMT-CAMD if an accurate prediction method is available, for example, a GC method or QSPR method.\textsuperscript{18} Otherwise, the ranking can be assessed a posteriori. To obtain a ranking of varying molecular structures, the integer-cuts are only applied to the molecular structures and not to the flowsheet configuration. However, the method is not limited to this integer-cut formulation and the flowsheet configuration can be also considered within the integer-cuts if necessary.

4.1 | Results of 1-stage CoMT-CAMD

The integrated design is performed considering the net present value $NPV$ as objective (Equation (8)). Initially, the relaxation problem is solved leading to a hypothetical optimal working fluid and process flowsheet, the target, with an objective function value of $NPV = 109,400\text{€}$. The flowsheet configuration of the target is the basic ORC without regeneration, turbine bleeding, or reheating. 1-stage CoMT-CAMD with integer-cuts is used to calculate a ranking of 10 working fluids (Table 3). The identified working fluids are mainly branched C5 alkanes and alkenes with regeneration as optimal flowsheet configuration. The optimal identified working fluid is 1-pentene with $NPV = 75,488\text{€}$, which is 31% lower than the target value. Further branched C5 alkenes and alkanes are identified on rank 2 to rank 8 with a similar economic performance as the optimal working fluid 1-pentene demonstrating the good performance of these families of working fluids ($NPV = 60,482\text{€}$–$72,624\text{€}$). For cyclopentane (rank 9) and 3,3-dimethyl-1-butene (rank 10), the net present value $NPV$ decreases significantly. On the one hand, no further promising branched C5 alkane or alkene is available in the design space due to the limited set of functional groups. The set of functional groups can be easily extended in future work. On the other hand, local optimal solutions can be identified since a local MINLP solver is used. Only for cyclopentane (rank 9), the basic flowsheet configuration is identified. Cyclopentane has a smaller heat capacity and the lower bound of the pressure level ($p_{\text{min}} = 1\text{ bar}$) is active leading to a higher condensation temperature. Consequently, if active regeneration is enforced for cyclopentane, only a comparatively small amount of heat is available for regeneration ($Q_{\text{reg}} = 99\text{ kW}$) leading to a process which is economically much less efficient ($NPV = 29,164\text{€}$).

Although the optimal flowsheet configuration of the target is the basic ORC, regeneration is selected for the promising real working fluids. The target for the basic ORC has a comparatively small heat capacity and nearly an isentropic line of saturated vapor leading to a low temperature at turbine outlet (Figure 4, target for basic ORC). In contrast, if active regeneration is enforced, the resulting target has a lower positive gradient of the line of saturated vapor (dry working fluid) leading to a higher temperature at turbine outlet, which benefits the heat regeneration (cf. Figure 4, target with regeneration). However, the net present value $NPV$ is 12% lower due to higher investment cost ($NPV = 96,268\text{€}$). The optimal real working fluids of the considered molecular design space have similar properties to the target with regeneration leading to an optimal flowsheet configuration with regeneration. However, the consideration of additional functional groups may lead to molecular structures with similar properties as the target for basic ORC and thus to optimal real working fluids with basic flowsheet configuration.

4.2 | Impact of the objective

The result of the integrated design of working fluids, processes, equipment, and flowsheet configurations depends on the objective function of the optimization problem. To illustrate this dependence, we repeat the integrated design with 1-stage CoMT-CAMD considering two alternative objectives:
1. the minimization of the specific investment cost \( SIC \) as an objective function commonly employed for the design of ORCs in the literature since fewer assumptions are necessary for cost parameters, which are often time and location dependent:\(^9\)

\[
\begin{align*}
&= f_2(x, \theta, w) = \frac{TCI}{P_{net}},
&= 21
\end{align*}
\]

2. the maximization of the net power output \( P_{net} \) as thermodynamic objective:

\[
\begin{align*}
&= f_3(x, \theta, w) = P_{net},
&= 22
\end{align*}
\]

\( \text{TABLE 3} \) Target and top 10 ranking of the working fluids identified with 1-stage CoMT-CAMD considering the net present value NPV as objective

| Rank | Name       | NPV (€) | \( P_{net} \) (kW) | \( Q_{reg} \) (kW) | \( w_{reg} \) | \( w_{reh} \) | \( w_{bl} \) |
|------|------------|---------|-------------------|------------------|-------------|-------------|-------------|
| —    | Target     | 109,400 | 161               | 0                | 0           | 0           | 0           |
| 1    | 1-Pentene  | 75,488  | 170               | 178              | 1           | 0           | 0           |
| 2    | Pentane    | 72,624  | 169               | 206              | 1           | 0           | 0           |
| 3    | 2-Methyl-1-butene | 71,820 | 168               | 165              | 1           | 0           | 0           |
| 4    | Isopentane | 70,586  | 170               | 221              | 1           | 0           | 0           |
| 5    | 3-Methyl-1-butene | 68,476 | 166               | 196              | 1           | 0           | 0           |
| 6    | 2-Pentene  | 67,309  | 165               | 150              | 1           | 0           | 0           |
| 7    | Neopentane | 62,789  | 171               | 268              | 1           | 0           | 0           |
| 8    | 2-Methyl-2-butene | 60,482 | 160               | 139              | 1           | 0           | 0           |
| 9    | Cyclopentane | 46,249 | 133               | 0                | 0           | 0           | 0           |
| 10   | 3,3-Dimethyl-1-butene | 24,909 | 150               | 225              | 1           | 0           | 0           |

Note: Additionally, the corresponding net power output \( P_{net} \), the heat flow for regeneration \( Q_{reg} \), and the binary structural decision variables \( w_{reg} \), \( w_{reh} \) as well as \( w_{bl} \) are shown.

which is simple to apply since it does not require equipment sizing and thus no transport properties of the working fluid. For these reasons, the net power output is often employed for CAMD of ORCs.\(^{17,21}\) Here, the lower bound of the minimal approach temperature in the heat exchangers is limited to a typical value of \( \Delta T_{\min} = 5 \text{K} \) since no trade-off between the objective function and the minimal approach temperature is reflected in the model.

For the specific investment cost \( SIC \) as the objective function, the target value is \( SIC = 3,343 €/kW \) (Table 4). The top five working fluids identified are again C5 alkanes or alkenes and have been also identified in the ranking maximizing the net present value (Table 3). The \( SIC \)-optimal working fluid is 2-pentene with specific investment cost of \( SIC = 3,488 €/kW \), which is 4.3\% higher than the target value. For the earlier optimization maximizing the net present value NPV (cf. Table 3), 2-pentene was also identified as rank position 6. Here, the annual operating costs for cooling or maintenance are additionally considered within the objective. Compared to minimizing the specific investment cost, maximizing the net present value leads to a 4.5 and 4.8\% higher net present value of the target and 2-pentene, respectively. Minimizing the specific investment cost \( SIC \) identifies the basic ORC flowsheet configuration for the target as well as for all identified real working fluids. Because the specific investment cost \( SIC \) does not consider the annual operating costs, the trade-off between lower cooling cost and higher regenerated heat is not captured by the objective and the regenerator is not selected in the optimal flowsheet configuration.

Considering the net power output \( P_{net} \) as objective, the target value is \( P_{net} = 182.6 \text{ kW} \) (Table 5). Again, the top five working fluids are C5 alkanes or alkenes and were identified earlier when maximizing the net present value (Table 3). The \( P_{net} \)-optimal working fluid is pentane with a net power output of \( P_{net} = 178.6 \text{ kW} \), which is 2.2\% lower than the target value. Pentane has rank 2 for maximization of the net present value NPV (cf. Table 3). However, for maximizing the net power output \( P_{net} \), the full flowsheet including regeneration,
Because all additional units in the flowsheet configuration increase the thermal efficiency, the full flowsheet configuration is selected leading to a high net power output and the total capital investment. Therefore, the net present value NPV of the target and pentane are negative with −13,387€ and −15, 390€, respectively. Thus, considering the total capital investment within the design of the flowsheet configuration is important to obtain economically efficient processes. The similar rankings for all three objective functions result from the small molecular design space due to the limited set of functional groups, which contains only eight possible molecular structures for the favorable C5 alkanes/alkenes. The rankings are expected to differ more strongly as soon as the set of functional groups is extended. However, also the results for the small design space show that both, the optimal working fluid and the optimal flowsheet configuration, differ for all objectives. Thus, the objective function has to be selected carefully.

### Table 4
Target and top five working fluids identified with 1-stage CoMT-CAMD considering the specific investment cost SIC as objective

| Rank | Name             | SIC (€/kW) | NPV (€) | $P_{\text{net}}$ (kW) |
|------|------------------|------------|---------|------------------------|
|      | Target           | 3,343      | 104,446 | 154                    |
| 1    | 2-Pentene        | 3,488      | 64,074  | 142                    |
| 2    | 2-Methyl-2-butene| 3,494      | 59,811  | 139                    |
| 3    | 1-Pentene        | 3,496      | 63,897  | 143                    |
| 4    | 2-Methyl-1-butene| 3,498      | 63,029  | 143                    |
| 5    | Pentane          | 3,521      | 55,842  | 140                    |

Note: Additionally, the corresponding net present value NPV and net power output $P_{\text{net}}$ are shown. The flowsheet configurations for regeneration, turbine bleeding, and reheating are not selected in the corresponding optimal flowsheet.

### Table 6
Optimal working fluid identified with 1-stage CoMT-CAMD based on a top five ranking depending on fixed flowsheet configurations for regeneration (reg), reheating (reh) and turbine bleeding (bl)

| $w_{\text{reg}}$ | $w_{\text{reh}}$ | $w_{\text{bl}}$ | Name             | NPV (€) |
|------------------|------------------|------------------|------------------|---------|
| 1                | 0                | 0                | 1-Pentene        | 75,488  |
| 0                | 0                | 0                | 1-Pentene        | 66,746  |
| 0                | 0                | 1                | 2-Methyl-1-butene| 65,829  |
| 1                | 0                | 1                | 1-PENTENE        | 50,910  |
| 1                | 1                | 0                | 1-Pentene        | 31,484  |
| 0                | 1                | 0                | 2-Methyl-1-butene| 18,698  |
| 0                | 1                | 1                | 2-Methyl-1-butene| 18,346  |
| 1                | 1                | 1                | 1-Pentene        | 6,524   |

Note: The net present value NPV is considered as objective and used to sort the list.

### Table 7
Optimal working fluid identified with 1-stage CoMT-CAMD based on a top five ranking depending on fixed flowsheet configurations for regeneration (reg), reheating (reh) and turbine bleeding (bl)

| $w_{\text{reg}}$ | $w_{\text{reh}}$ | $w_{\text{bl}}$ | Name             | SIC (€/kW) |
|------------------|------------------|------------------|------------------|-------------|
| 0                | 0                | 0                | 2-Pentene        | 3,488       |
| 1                | 0                | 0                | 1-Pentene        | 3,572       |
| 0                | 0                | 1                | 2-Pentene        | 3,595       |
| 1                | 0                | 1                | 1-Pentene        | 3,669       |
| 0                | 1                | 0                | 2-Pentene        | 3,768       |
| 1                | 1                | 0                | 1-Pentene        | 3,797       |
| 0                | 1                | 1                | 2-Methyl-1-butene| 3,838       |
| 1                | 1                | 1                | 2-Methyl-1-butene| 3,895       |

Note: The specific investment cost SIC is considered as objective and used to sort the list.
configuration: the ORC with regeneration is optimal for the net present value NPV (Table 6) and the basic ORC is optimal for the specific investment cost SIC (Table 7). While the economics are comparable for the basic ORC flowsheet, the ORC with regeneration and the ORC with turbine bleeding, the economic benefit is significantly lower for the other flowsheet configurations. In particular, the net present value NPV can be increased by a factor of more than 11 by selecting the optimal flowsheet configuration (Table 6). In contrast, the achieved reduction in the specific investment cost is lower than 11% (Table 7).

For the net present value NPV, 1-pentene is identified as the optimal working fluid for five flowsheet configurations and 2-methyl-1-butene for three flowsheet configurations. For the specific investment cost SIC, 2-pentene and 1-pentene are identified as the optimal working fluid for three flowsheet configurations, respectively, and 2-methyl-1-butene for 2 flowsheet configurations. Thus, the optimal working fluid depends on the flowsheet configuration and a systematic integrated selection of working fluid and flowsheet configuration is required to obtain overall optimal solutions. Such a systematic integrated selection is enabled by the presented 1-stage CoMT-CAMD method.

To calculate a ranking of five working fluids, the presented method took 48 min for the net present value NPV and 26 min for the specific investment cost SIC using an Intel-Xeon CPU with 3.0 GHz and 64 GB RAM. These times include the design of the flowsheet configuration. In contrast, the enumerative integrated design for each flowsheet configuration took in total 8 hr 2 min for the net present value NPV and 7 hr 33 min for the specific investment cost SIC. Thus, integrating flowsheet design into the design problem saves 90% and 94% of computational resources, respectively. The time for the enumerative optimization could be reduced by parallelization of the individual optimizations. However, the longest individual calculation took 91 min for the net present value NPV and 69 min for the specific investment cost SIC such that the presented integrated design still saves 48% and 62% of the computational resources, respectively. The comparatively large computational time for fixed flowsheet configurations occurs for complex flowsheet configurations, which are avoided by the superstructure-based integrated design. Thus, the presented 1-stage CoMT-CAMD method is an efficient and accurate method for the integrated design of working fluids, processes, equipment, and flowsheet configurations.

5 | CONCLUSIONS

In this work, we integrate superstructure-based design of flowsheets into the design of processes and molecules based on the 1-stage CoMT-CAMD method. For this purpose, a CAMD formulation is directly linked to a superstructure of the process model. The superstructure of the process enables us to optimize the flowsheet configuration based on binary structure decision variables and additional continuous process degrees of freedom. Detailed models for the sizing of the equipment are considered to capture the trade-off between higher thermodynamic efficiencies and higher total capital investment arising from the optional flowsheet configurations. The PC-SAFT EoS is used as consistent thermodynamic model to calculate both, equilibrium and transport properties of the molecules. The superstructure of the processes is defined in the flowsheeting software gPROMS ProcessBuilder using model libraries and easy drag-and-drop flowsheeting. The resulting method enables the identification of the optimal molecule and flowsheet configuration as well as the corresponding optimal process and equipment sizes in a single optimization problem.

The presented method is demonstrated for the design of an ORC for waste heat recovery considering regeneration, turbine bleeding, and reheating as options for the flowsheet configuration. 1-stage CoMT-CAMD is used to identify the most promising working fluids, which maximize the net present value. We observe different flowsheet configurations for the top 10 working fluids, which clarify that optimizing the flowsheet configuration cannot be solved in an independent subproblem from the design of molecules and process settings.

For the studied low-temperature case study, 1-pentene is identified as optimal working fluid in an ORC with regeneration. However, the optimal working fluid and flowsheet configuration are shown to differ for optimization with respect to of the net present value, the specific investment cost and the net power output. An enumerative design of each possible flowsheet configuration shows that the optimal working fluid depends on the flowsheet configuration emphasizing the significance of an integrated design method. Furthermore, we show that our integrated design method is computationally more efficient than the enumerative optimization of each flowsheet configuration with savings of computational resources of up to 94%. Thus, our presented method is shown to be efficient for the integrated design of molecules, processes, equipment, and flowsheet configurations.

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SUPPORTING INFORMATION
Additional supporting information may be found online in the Supporting Information section at the end of this article.

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