Multi-objective thermo-economic optimization of organic Rankine cycle (ORC) power systems in waste-heat recovery applications using computer-aided molecular design techniques

Luuk M. T. van Kleef, Oyeniyi A. Oyewunmi* and Christos N. Markides

Clean Energy Processes (CEP) Laboratory, Department of Chemical Engineering, Imperial College London, London SW7 2AZ, U.K.

Abstract

In this paper, we develop a framework for designing optimal organic Rankine cycle (ORC) power systems that simultaneously considers both thermodynamic and economic objectives. This methodology relies on computer-aided molecular design (CAMD) techniques that allow the identification of an optimal working fluid during the thermo-economic optimization of the system. The SAFT-$\gamma$ Mie equation of state is used to determine the necessary thermodynamic properties of the designed working fluids, with critical and transport properties estimated using empirical group-contribution methods. The framework is then applied to the design of sub-critical and non-recuperated ORC systems in different applications spanning a range of heat-source temperatures. When minimizing the specific investment cost (SIC) of these systems, it is found that the optimal molecular size of the working fluid is linked to the heat-source temperature, as expected, but also that the introduction of a minimum pinch point constraint that is commonly employed to account for inherent trade-offs between system performance and cost is not required. The optimal SICs of waste-heat ORC systems with heat-source temperatures of 150 °C, 250 °C and 350 °C are £10,120/kW, £4,040/kW and £2,910/kW, when employing propane, 2-butane and 2-heptene as the working fluids, respectively. During a set of MINLP optimizations of the ORC systems with heat-source temperatures of 150 °C and 250 °C, it is found that 1,3-butadiene and 4-methyl-2-pentene are the best-performing working fluids, respectively, with SICs of £9,640/kW and £4,000/kW. These substances represent novel working fluids for ORC systems that cannot be determined a priori by specifying any working-fluid family or by following traditional methods of testing multiple fluids. Interestingly, the same molecules are identified in a multi-objective optimization considering both the total investment cost and net power output. These findings highlight the power of this approach as it enables the selection of novel working fluids while optimizing ORC systems using single or multiple thermo-economic performance indicators.

Key words: multi-objective optimization; organic Rankine cycle; thermo-economic; waste heat recovery; working fluids; computer-aided molecular design (CAMD)

* Corresponding author. Telephone: +44 (0)20 759 41601. E-mail: o.oyewunmi@imperial.ac.uk
Nomenclature

Abbreviations
CAMD Computer-aided molecular design
EoS Equation of state
GC Group-contribution
MINLP Mixed-integer non-linear programming
MOO Multi-objective optimization
NLP Non-linear programming
NSGA-II Non-dominated sorting genetic algorithm-II
ORC Organic Rankine cycle
PEC Purchased equipment cost
SAFT Statistical associating fluid theory
SIC Specific investment cost
SPEC Specific purchased equipment cost
TIC Total investment cost

Symbols
$A_s$ Heat exchange surface area [$m^2$]
$C^{BM}$ Base bare module costs [USD]
$C_{BM}$ Bare module costs [USD]
$c_p$ Specific heat capacity [J/(kg K)]
$D$ Diameter [m]
$f_0$ Friction factor [-]
$g$ Gravity constant [m/s²]
$G$ Mass flux [kg/m²]
$h$ Specific enthalpy [J/kg]
$k$ Thermal conductivity of solid tube material [W/(m K)]
$L$ Length [m]
$\dot{m}$ Mass flow rate [kg/s]
$P$ Pressure [Pa]
$P_r$ Reduced pressure [-]
$\dot{Q}$ Heat transfer rate [W]
$Re$ Reynolds number [-]
$s$ Specific entropy [J/kg K]
$T$ Temperature [K or °C]
$U$ Overall heat transfer coefficient [W/m²]
$v$ Velocity [m/s]
$\dot{W}$ Work rate [W]
$z$ Normalized degree of superheating [-]

Greek
$\alpha$ Heat transfer coefficient [W/(m² K)]
$\eta$ Efficiency [-]
$\lambda$ Thermal conductivity [W/(m K)]
$\mu$ Dynamic viscosity [Pa s]
\( \rho \) Mass density \([\text{kg/m}^3]\)

\( \sigma \) Surface tension \([\text{N/m}]\)

\( \omega \) Accentric factor \([-\]\

### Subscripts

- \( a \) Accelerational
- \( c \) Heat sink
- \( \text{cond} \) Condenser
- \( \text{cr} \) Critical property
- \( \text{evap} \) Evaporator, Evaporation
- \( f \) Frictional
- \( h \) Heat source
- \( i \) Equipment unit \( i \)
- \( \text{in} \) Inlet
- \( \text{lm} \) Log mean
- \( L \) Liquid phase
- \( n, n \) Net, Number of Carbon atoms
- \( \text{out} \) Outlet
- \( P \) Pressure
- \( \text{pinch} \) Pinch point
- \( \text{pump} \) Pump
- \( r \) Reduced property
- \( s \) Isentropic
- \( \text{sat} \) Saturated
- \( \text{th} \) Thermal
- \( \text{turb} \) Turbine
- \( V \) Vapour phase
- \( \text{wall} \) Properties at wall of heat exchanger
- \( \text{wf} \) Working fluid
- \( x \) Internal point in heat exchanger
- \( 0 \) Reference value

### Superscripts

- \( \text{lo} \) Lower bound
- \( \text{up} \) Upper bound
1 Introduction

The utilization of low- and medium-grade heat, such as from waste-heat streams and a variety of renewable heat sources such as solar, geothermal and biomass, can play an important role in meeting the growing global demand for clear and secure energy while adhering to increasingly stringent environmental and sustainability targets. Converting these heat sources into electrical power has the potential to increase energy efficiency, thereby reducing primary fuel use and emissions in many applications [1–3]. Currently, a range of technologies are being considered for such heat conversion applications, include organic Rankine cycle (ORC) engines [4,5], microturbines [6], thermoelectric generators [7,8], but also others such as Stirling [9–11] or Ericsson engines, and thermofluidic oscillators such as the NIFTE [12–14] or Up-THERM heat converter [15–17]. Of these, ORC systems are particularly well-suited to the conversion of heat at temperatures below 400–500 °C, and can be more effective than steam turbines and other competing technologies at such temperatures and at smaller scales [2,18]. ORC systems have already been implemented commercially at scales from a few kW to tens of MW for the conversion of waste heat, solar heat and heat from biomass combustion, and have been used to increase the energy efficiency of industrial facilities through waste heat recovery for power generation [3,19].

The identification of optimal ORC system designs and specifications has received significant attention in the literature, and computer-aided optimization techniques offer the opportunity to apply effective and systematic solutions in this regard. Amongst a number of similar studies, Bao and Zhao [20] present an excellent overview of parametric and optimization studies and recommend suitable working fluids for different ORC applications. Performing such thermodynamic optimization exercises has been crucial to advancing our understanding of the potential of ORC technology and of the thermodynamic challenges and opportunities in a wide variety of applications, however, using preselected sets of working fluids while excluding economic considerations can result in the exclusion of alternative fluids, which might achieve better overall system performance or lower costs.

The development of computer-aided molecular design (CAMD) methods, which introduce the working fluid substance as an unknown element within the overall search for an optimal ORC system, has led to the possibility of combining systematically the selection or design of the working fluid with ORC system design and operational parameters (pressures, temperatures, etc.), thereby omitting the subjective preselection of conventional approaches [21,22]. In CAMD approaches, molecules are described as combinations of smaller structural groups (e.g., –CH₃, or =CH–) such that, theoretically, any arbitrary molecule can be described as a collection of such groups, as long as that all relevant groups are incorporated in the decision space.

Many authors have used CAMD techniques for the optimization of ORC systems by using semi-empirical group-contribution (GC) methods and equations of state (EoS). Of note is the work by Papadopoulos et al. [23,24], who performed a two-step optimization study in which an initial set of potentially well-performing working fluids was generated using molecular thermodynamic and transport properties as objectives. In a subsequent step, the ORC system of interest was optimized with the set of promising working fluids, and a ranking of the fluids was presented. In a different study by the same authors, a similar CAMD approach was used to assess mixtures of working fluids in ORC systems [25]. Palma-Flores et al. [26] applied a CAMD
approach to the identification of a working fluid in a waste-heat recovery application, while simultaneously selecting an optimal cycle configuration. A long list of novel fluids was identified, which outperformed conventional working fluids in terms of efficiency or power output. In more recent work, Schwöbel et al. [27] and Preißinger et al. [28] developed a framework capable of screening a large database of fluid candidates. In two subsequent steps, millions of compounds were screened and fluid selection was made based on quantum-mechanical and thermodynamic calculations, after applying an empirical EoS for the latter. A parametric maximization of the power output was conducted leading to the final selection of the best working fluids. In Cignitti et al. [29] the thermodynamic performance of a recuperated ORC system was optimized, with considerations of the associated heat-exchanger requirements. Su et al. [30] integrated EoS GC methods into a thermodynamic ORC model. When comparing the performance predictions using these GC methods with reference data taken from REFPROP [31], deviations below 10% were reported, suggesting that these methods may be sufficient in many cases for predicting working fluid properties in the context of ORC system optimization. In further work by the same authors, CAMD optimization was performed using this framework with the objective of maximizing the system power output [32].

Although much has been learnt from these previous approaches, using REFPROP or similar EoSs limits solutions to a limited number of well-known fluids for which reliable data exists in the thermodynamic property database of interest, and further, an inherent disadvantage of empirical GC EoSs arises from their potentially reduced accuracy relative to molecular thermodynamics-based EoSs, in particular relating to predictions of second-order derivative quantities such as the specific enthalpy ($h$) and specific heat capacity ($c_p$) [33], especially when conditions or substances are assessed for which no or few experiments have been performed. The recent acceleration in the introduction of regulations relating to the use of suitable fluids and the resulting ever more frequent turnaround of suitable chemicals, along with the growth in the development of new chemicals, have led to a particular interest in methods that can be relied upon to provide accurate property predictions with little or no experimental data. The statistical associating fluid theory (SAFT) offers a way to circumvent these limitations to a large extent, as it enables thermodynamic property predictions even when these are beyond the ranges for which experimental data is available [34].

Several SAFT formulations have been developed, including PC-SAFT [35], SAFT-VR Mie [36] and SAFT-γ Mie [34]. PC-SAFT is based on a perturbed-chain model, representing molecular subgroups as hard spheres [35], whereas SAFT-VR Mie and SAFT-γ Mie both use hetero-nuclear fused chain models where a Mie pair potential is used to describe the interaction between segments. Both PC-SAFT and SAFT-γ Mie are compatible with GC approaches. Dufal et al. [37] showed that the SAFT-γ Mie EoS is capable of accurate predictions of the vapour-liquid equilibrium data of pure components and mixtures of several hydrocarbon families. Of interest here, is that second derivative properties can also be predicted with high accuracy by SAFT-γ Mie. A detailed description of SAFT-γ Mie is presented in the article of Papaioannou et al. [34].

The SAFT-VR Mie EoS was employed by Oyewunmi et al. [4,38,39], in order to investigate the use of working fluid mixtures in ORC systems, and SAFT-based GC EoSs have been applied specifically to CAMD
optimization studies of ORC systems. Of note here is the on-going work at Aachen, e.g., Lampe et al. [40,41], who have developed a two-stage CAMD-ORC framework with the PC-SAFT EoS referred to as ‘continuous-molecular targeting CAMD’ (CoMT-CAMD). Using this approach, the ORC system and working fluid are optimized first as a non-linear programming (NLP) problem; in a second step, a working fluid is chosen and evaluated in a parametric optimization. Following this work, Schilling et al. [42] proposed a single-stage CoMT-CAMD optimization approach, where ORC system parameters and the working fluid are selected simultaneously during optimization, which is classified as a mixed-integer non-linear programming (MINLP) problem. Both the maximum net power output and minimum temperature at the heat source outlet were used as optimization objectives. Economic evaluations were, however, not incorporated into these advanced optimization attempts. The major findings in this work suggest that not only existing working fluids (with data already available in various databases), but also novel working fluids can appear as promising solutions.

The studies presented above focused on the optimal thermodynamic performance of ORC systems, in some cases while considering costs. Thermodynamic performance is of great importance, however, it is only one consideration in the implementation of ORC systems [43]; a balance between both performance and economic feasibility is required for the determination of an optimal system that stands the best chance of practical implementation [44]. The economic feasibility of new technologies is strongly determined by the upfront investment costs, with capital cost estimations receiving considerable attention in this context [45]. Such economic indices have been considered recently in CAMD efforts relating to ORC systems. Schilling et al. [46] devised a CAMD-ORC optimization framework based on PC-SAFT, where both the total investment cost and the power generated were used as objective functions. A deterministic MINLP solver was used to optimize the system for a waste-heat recovery application. This work showcases the merit of integrating detailed equipment design and costing models in a CAMD-ORC optimization model, and the possibility of making thermo-economic trade-offs by considering multiple objectives simultaneously.

More recently, White et al. [47] proposed a framework to assess both the thermodynamic and economic performance of waste-heat recovery ORC systems. In this work, a CAMD-ORC optimization was performed first in order to identify systems that maximize power generation. Subsequently, the investment costs of these systems were estimated through component sizing models. Empirical GC methods were used to estimate relevant transport properties such as thermal conductivity ($\lambda$), dynamic viscosity ($\mu$) and surface tension ($\sigma$), as these cannot be predicted using SAFT-$\gamma$ Mie. It was found that working fluids that maximize the power output from the ORC system generally require large heat exchanger areas, and it was concluded that working-fluid selection based on SIC minimization or power output maximization can result in different solutions. This post-optimization cost determination provides valuable insight into the trade-offs between optimal thermodynamic performance and the implications this has on the system’s cost and its broader economic characteristics. However, economic/cost objectives were not considered explicitly during the optimization procedure.

The integration of a SAFT-based EoS within a CAMD-ORC optimization framework has the potential to identify novel working fluids that lead to enhanced thermodynamic performance. However, there is a need to
develop advanced frameworks that include cost considerations along with the thermodynamic performance of the optimized systems. Thus, the novelty and scientific contributions of the present work, and where it goes beyond previous efforts, such as that by White et al. [47], arise from:

- including detailed equipment sizing and system cost estimation models in the current framework;
- developing an extended thermo-economic SAFT-CAMD framework that allows for simultaneous ORC system design and working-fluid optimization, while accounting for both thermodynamic performance and system cost optimization;
- deriving non-traditional and novel working fluids, from constituent molecular groups, for ORC systems via the formulation of MINLP and multi-objective cost-power optimization problems.

The new framework is then applied to subcritical and non-recuperated ORC systems in waste-heat recovery applications. A range of waste-heat sources are considered, in order to examine the effect of the heat-source temperature on optimal working-fluid and system design, while analyses of cycle and system operating conditions on optimal system designs are also presented. The optimal designs are characterised by a number of single objective functions and multi-objective combinations of power output, total and specific investment costs, while also considering the effect of the choice of objective function on the optimal system and working fluid design.

2 Methodology and Problem Definition

The full thermo-economic SAFT-CAMD ORC model is implemented in the gPROMS software environment v5.0.1 [48] and optimizations are performed in MATLAB (R2017a) [49]. The framework consists of a thermodynamic cycle description, heat exchanger sizing models and correlations to estimate the required capital costs of the system components. The molecular groups considered are \(-\text{CH}_3, -\text{CH}_2-, >\text{CH}-, >\text{C}<, =\text{CH}_2\) and \(=\text{CH}-\), where \(-, =\) and \(>\) denote single, double and two single bonds respectively. The working fluid is defined by assigning integer values to each molecular group, representing the quantity of each group present in the working fluid molecules. Beyond the integer variables used by the GC method to describe the working fluid, six continuous decision variables are varied during the optimization, namely: (i) the reduced pressure in the evaporator \((P_r)\), (ii) the internal temperature difference in the evaporator \((\Delta T_x)\), (iii) the normalized degree of superheating \((z)\), (iv) the condensing temperature \((T_1)\), and (v,vi) the velocities of the working fluid in the evaporator \((v_{\text{evap}})\) and the condenser \((v_{\text{cond}})\). These variables are described in the following section.

2.1 Thermodynamic cycle model

The purpose of this sub-model is to calculate thermodynamic performance indicators of the system such as the net power output \((\dot{W}_n)\) and the overall thermal efficiency \((\eta_a)\), and to determine the outlet conditions of the heat-source and heat-sink streams. Furthermore, the duty and various temperatures through the two heat exchangers are determined, which are used to size the heat exchangers. A typical temperature-specific
entropy \((T-s)\) diagram of the subcritical, non-recuperated ORC considered in this work is shown in Fig. 1a. A corresponding schematic representation of the ORC system and its main components is shown in Fig. 1b.

At each of the state points in Fig. 1a, the thermodynamic properties such as \(s\), \(c_p\), \(h\) and density \((\rho)\) are estimated using the SAFT-\(\gamma\) Mie EoS. The thermodynamic model used in this study is based on the work by White et al. [50], which was validated by comparison with another CAMD-ORC optimization study performed by Schilling et al. [42]. For completeness, a brief overview of the thermodynamic model is provided here.

![Figure 1: (a) General T-s diagram of a subcritical, non-recuperated ORC. States 2, 3, 4 and 5 are all at high pressure, and the working fluid phase at these states is subcooled liquid, saturated liquid, saturated vapour and superheated vapour, respectively. States 6, 7 and 1 are all at low pressure, and the working fluid phase at these states is superheated vapour, saturated vapour, saturated liquid and subcooled liquid, respectively. The red and blue lines denote the profiles of the heat source and cooling utility, respectively, during heat exchange, and ‘X’ denotes the critical point. (b) Schematic illustration of a basic subcritical and non-recuperated ORC system. The green line denotes the working fluid flows. Points 1, 2, 5 and 6 correspond to the states from Fig. 1a.](image)

It is assumed that the working fluid is a saturated liquid at State 1, thus its thermodynamic state is determined by the condensation temperature \(T_1\), which directly fixes \(P_1\), \(P_6\) and \(P_7\), since condensation is in the first instance assumed to be an isobaric process (we discuss this below Eq. 2 and in Section 2.3.2). Irreversibilities that occur during the pumping process are accounted for by defining an isentropic pumping efficiency \((\eta_{\text{s,pump}})\).

The evaporator (subscript ‘evap’) is divided into preheating \((\text{States } 2 \rightarrow 3)\), evaporating \((\text{States } 3 \rightarrow 4)\) and vapour superheating \((\text{States } 4 \rightarrow 5)\) sections. The decision variable \(\Delta T_x\) (temperature difference) and outlet temperature \(T_5\) as determined from the normalized degree of superheating \((z)\) are defined from:

\[
\Delta T_x = T_{h,x} - T_3, \quad (1) \quad T_5 = T_4 + z(T_{h,in} - T_4). \quad (2)
\]

The position in the cycle of temperatures \(T_{h,x}\) and \(T_3\) are shown in Fig. 1a. The variable \(z\) varies between 0 and 1, indicating either no \((z = 0)\) or the theoretical maximum amount of superheating \((z = 1)\). \(\Delta T_x\) represents the temperature difference between the heat source and the working fluid, at the saturated liquid point in the evaporator. The variable \(\Delta T_{\text{pinch}}\) is used to describe the smallest temperature difference between the hot and
cold streams in the evaporator and condenser. This pinch point can occur at the inlets, outlets or internally in the heat exchangers. Thus, $\Delta T_x = \Delta T_{\text{pinch}}$ if the pinch point occurs internally in the evaporator and at the saturated liquid point; otherwise, $\Delta T_x > \Delta T_{\text{pinch}}$.

The expansion process (States 5 $\rightarrow$ 6) is simulated in a similar way to the pumping process, and irreversibilities are accounted for by defining an isentropic turbine efficiency ($\eta_{\text{isent}}$), and the condenser (subscript ‘co’) is divided into a desuperheating section, where the superheated vapour is cooled down to the saturation temperature (States 6 $\rightarrow$ 7), and a condensing section (States 7 $\rightarrow$ 1); see Fig. 1a.

For simplicity and as is common practice in such studies, pressure drops are neglected in the thermodynamic cycle. However, to overcome the pressure drops, more work is required by the pump and less power is generated by the turbine. Therefore, the design of the heat exchangers which determines these pressure drops, does not only affect the cost of these components but directly influences system performance. To account for the pressure drop in the evaporator ($\Delta P_{\text{evap}}$), the pump delivers additional work by increasing the pressure from $P_1$ to $P_2 + \Delta P_{\text{evap}}$ (instead of just from $P_1$ to $P_2$). Similarly, to account for the pressure drop in the condenser ($\Delta P_{\text{cond}}$), the working fluid can only expand from $P_5$ to $P_6 + \Delta P_{\text{cond}}$ (instead of from $P_5$ to $P_6$). This ensures that the working fluid can overcome $\Delta P_{\text{cond}}$ and leaves the condenser at a pressure of $P_1$. The rate of electrical power consumption by the pump ($W_{\text{pump}}$) and rate of power generation by the turbine ($W_{\text{turb}}$) are calculated from the enthalpy differences over these processes, while considering pressures corrected for the pressure drops:

$$W_{\text{pump}} = m_{\text{wf}}(h_{\text{pump}} - h_1), \quad (3)$$
$$W_{\text{turb}} = m_{\text{wf}}(h_5 - h_{\text{turb}}), \quad (4)$$

where $h_{\text{pump}}$ and $h_{\text{turb}}$ denote the specific enthalpies of the working fluid at the outlets of the pump and turbine, corrected for pressure drops in the heat exchangers. Finally, the rate of net power generation ($W_n$) is given by:

$$W_n = W_{\text{turb}} - W_{\text{pump}}. \quad (5)$$

### 2.2 Group-contribution (GC) methods and validation

The employment of molecular groups to define working fluids requires the use of GC methods to determine molecular properties. Critical properties (subscript ‘cr’), such as $P_{\text{cr}}$ and $T_{\text{cr}}$, as well as transport properties such as $\mu$, $\lambda$ and $\sigma$, cannot be obtained through SAFT-$\gamma$ Mie. These transport properties influence heat/mass transfer, and are required to estimate heat transfer and pressure drops. Methods for the prediction of $\mu$, $\lambda$ and $\sigma$ do exist, that link these to thermodynamic fluid properties, which can be accurately predicted by SAFT-$\gamma$ Mie. In general, predictive correlations for $\mu$ and $\lambda$ are derived for a specific thermodynamic phase. Therefore, distinct correlations are employed for the liquid and vapour phases (subscripts ‘L’ and ‘V’, respectively):

- $P_{\text{cr}}$, $T_{\text{cr}}$ and critical molecular volume ($V_{\text{cr}}$): Joback and Reid [51].
- Accentric factor ($\omega$): Ambrose and Walton [52], with vapour pressure correlation by Pitzer [53].
- $\mu_L$: Joback and Reid for $n$-alkanes and unbranched alkenes [51]. Sastri and Rao for branched alkanes [54].
• $\mu_V$: Reichenberg [55,56]. In this work, only hydrocarbon molecules are considered, which generally have a low or non-existent dipole moment [43], thus, the dipole moments are assumed to be zero which agrees with the GC dipole moment prediction method by Sheldon et al. [44].

• $\lambda_L$: Sastri and Rao [53,57]; $\lambda_V$: Chung [58,59].

• $\sigma$: Sastri and Rao [60]. This method can be used to predict $\sigma$ for saturated liquids only.

The exact form of these correlations can be found in Ref. [50]. The implementation of these semi-empirical methods is straightforward and little computational effort is required to estimate fluid properties. However, a high degree of accuracy is not guaranteed for all substances and conditions. The use of such GC methods in an ORC framework has been explored [50,61], e.g., by comparing predicted property values against reference data from REFPROP [31] for various hydrocarbons. A reasonable agreement was reported for the estimation methods of $\mu$ and $\lambda$ for vapours and liquids at low temperatures. However, at high pressures and near-boiling temperatures, the deviations increased [61]. Further, the prediction accuracy for $\sigma$ varied between fluids. Accurate results were obtained for some hydrocarbons, but large deviations for were reported others, e.g., up to 44% for isobutane [61].

A further comparison is made between the $A_s$ and SIC values as determined with GC methods and REFPROP data in Ref. [61]. This was done for optimized systems with $n$-butane, isohexane and 1-propene with a $T_{h,in}$ of 150 °C, 250 °C and 350 °C, respectively. Isobutane with a $T_{h,in}$ of 350 °C was also assessed, to see the influence of an inaccurate $\sigma$ prediction at high temperatures. An underestimation of the SIC between 0.7% and 4.3% was reported, which compared to the inaccuracy introduced by the necessary application of cost correlations (±30%), is considered a relatively small uncertainty [62]. Given also that GC methods allow the assessment of fluids for which no data is available, makes their use in an ORC system optimization context of great interest.

2.3 Heat exchanger sizing

The evaporator and condenser are modelled as double-pipe tubular heat exchangers, with the working fluid flowing in the inner tube and the heat source/sink flowing counter-currently through the annulus. This type of heat exchanger is suitable for small to medium-scale applications and is associated with relatively low capital costs due to its simple design [63,64]. Furthermore, the temperature profiles achieved in these heat exchangers is compatible with the profiles assumed in the thermodynamic model described earlier (see Fig. 1a).

The decision variables related to the heat exchangers are the two velocities ($v$) of the working fluid in these components, and specifically the bulk liquid velocity $v_{\text{evap}}$ at the inlet of the preheating section of the evaporator, and bulk liquid velocity $v_{\text{cond}}$ at the outlet of the condensing section of the condenser. Based on these velocities, the mass flow rates, properties of the fluids and diameters of the inner and outer pipes of the heat exchangers are obtained. The inner pipe is assumed to be 3.68-mm thick and made from carbon steel with a thermal conductivity ($k$) of 60 W/(mK), which is typical for double-pipe heat exchangers used at moderate pressures [64,65].
The following equations are used to size the heat exchangers:

\[
\dot{Q} = UA_s \Delta T_{lm},
\]

\[
\frac{1}{U} = \frac{1}{\alpha_{in}} + \frac{D_{out}}{D_{in}} \frac{1}{\alpha_{out}} + \frac{D_{out}}{2k} \ln \left( \frac{D_{out}}{D_{in}} \right),
\]

where \( \dot{Q} \) denotes the heat flow rate (in W), \( U \) the overall heat transfer coefficient (in W/(m\(^2\)K)), \( \Delta T_{lm} \) the log-mean temperature difference between the two streams (in K), \( \alpha \) the convective heat transfer coefficients (in W/(m\(^2\)K)), \( D \) the diameters (in m), and the subscripts ‘in’ and ‘out’ refer to the inner and outer surfaces of the pipe, respectively. Depending on the phase of the working fluid, different correlations for \( \alpha \) are used.

### 2.3.1 Heat transfer coefficients

Throughout the heat exchangers it is assumed that the heat source and sink streams do not undergo phase change and remain in the liquid phase; furthermore, in the preheating section the working fluid is present as a single-phase liquid flow, and in the superheating and desuperheating sections the working fluid flows as a single-phase vapour. In these single-phase flow sections, \( \alpha \) is determined by the well-known Dittus-Boelter correlation [66]. In the two-phase (evaporating and condensing) heat-exchanger sections, the heat exchangers are divided into ten subsections of equal duty, within which linear temperature profiles are assumed for the two fluid streams. In each subsection, the values of \( \alpha_{in}, \alpha_{out}, U \) and \( \Delta T_{lm} \) are determined, and these are used to calculate an area for that subsection. The total heat exchanger area \( A_s \) is then equal to the summation of the ten separate subsection areas.

Often, correlations to determine \( \alpha \) in a two-phase flow are derived by fits to experimental data obtained from a variety of operating conditions and fluids. A complication that arises in this approach is that the correlations are not guaranteed to be (equally) reliable for all fluids of interest. To address this problem, multiple two-phase correlations for \( \alpha_{in} \) are used. In the evaporating heat-exchanger section, the asymptotic correlations by Chen [67], Dobson et al. [68], Steiner and Taboruk [65] and Liu and Winterton [69], which employ the nucleate boiling correlations of Cooper [63] and Gorenflo [65] are hereby employed. The area of each subsection is calculated by using the four distinct correlations for \( \alpha_{in} \), and an average area is obtained for a subsection. In the condensing section, a similar approach is used to calculate an average area for each subsection, based on the correlations by Shah [70,71], Chaddock and Chato [63] and Boyko and Kruzhilin [72]. The correlations for single and two-phase \( \alpha \) are shown in Appendix A.

### 2.3.2 Pressure drops

In this study, gravitational pressure changes are neglected as the flows in the heat exchanger channels are assumed to be horizontal, and only acceleration and frictional pressure drops are considered. The single-phase frictional pressure drop per unit length in each heat exchanger subsection is calculated by:
\[
\frac{dP}{dx}_f = -\frac{4f_0}{D_{\text{in}}} \left( \frac{\rho v^2}{2} \right),
\]
where the subscript ‘f’ denotes frictional and \( f_0 \) is the friction factor and \( Re \) the Reynolds number. The pressure drop \( \Delta P_l \) in each subsection is then obtained by multiplying the length of each subsection with the differential pressure drop per unit length from Eq. 8.

Similarly, in the two-phase flow sections of the heat exchangers, the frictional pressure drop is calculated by using the correlations proposed by Friedel [73], and also, the acceleration pressure drop (\( \Delta P_a \)) component experienced over an entire phase-change region (which is not split into subsections) is calculated from:

\[
\Delta P_a = G^2 \left( \frac{1}{\rho_{\text{out}}} - \frac{1}{\rho_{\text{in}}} \right),
\]
where \( G \) denotes the mass flux and \( \rho_{\text{in}} \) and \( \rho_{\text{out}} \) the working fluid density at the inlet and outlet of this region.

### 2.4 Capital cost estimation and validation

A common indicator used in preliminary economic assessments of ORC systems is the specific investment cost (SIC). This metric represents the total investment cost (TIC) of the system per rated kW of generated power:

\[
\text{SIC} = \frac{TIC}{W_n},
\]

The capital cost estimation technique developed by Guthrie [74] relates all system costs back to the costs of major equipment/components. The ‘base bare module cost’ (\( C_{0BM,i} \)) is the costs of the major component \( i \), when it is operating at ambient pressure and constructed from standard materials. To derive the ‘bare module cost’ (\( C_{BM,i} \)), multiplier factors for pressure (\( F_{p,i} \)) and materials (\( F_{M,i} \)) are used, which account for any non-ambient operating pressure and non-standard construction materials. This results in a \( C_{BM,i} \) with an expected uncertainty of ±30% [43]. The aim of this study is to compare the relative costs of different ORC systems, rather than to obtain detailed and accurate cost estimations. Therefore, the Guthrie method is deemed sufficient and is applied to determine the TIC.

To account for cumulative inflation since the development of the aforementioned correlations, the ‘chemical engineering plant cost index’ (CEPCI) is used, of which all relevant values are shown in Table B.3 in Appendix B. All costs are converted to 2017 values. Finally, the TICs are determined from:

\[
TIC = 1.18 \sum_i C_{BM,i},
\]
where the multiplier of 1.18 is a combined contingency factor and contractor fee [75].

The major components in an ORC system are the evaporator and condenser (both divided into single- and two-phase sections; see Fig. 1a and Section 2.3), the pump, the turbine and the generator. Separate correlations are used for the two-phase heat-exchanger sections to account for their higher costs with respect to the single-phase sections. Turton [76] and Seider et al. [77] provide different sets of correlations for estimating \( C_{0BM,i} \) (and \( F_{p,i} \),...
for each equipment component $i$ in USD. In this study, it was found that a combination of these correlations provided the best agreement with actual ORC cost data. The correlations and parameters which are used in this study to determine the cost of each component are detailed in Tables A.1 and A.2 in the Appendix.

To validate the costing methodology, the ‘specific purchased equipment costs’ (SPEC) values of twelve optimized ORC systems, presented in the results section of this paper, are compared to a non-exhaustive list of cost data of commercial waste-heat recovery ORC systems recovered from Refs. [43] and [78]. For each optimized ORC system, the SPEC is calculated using three distinct sets of correlations: (i) those from Turton [76], (ii) those from Seider et al. [77], and (iii) a combination of correlations as presented in Tables B.1 and B.2 in Appendix B. These results are presented in Fig. 2.

![Image of a graph showing the comparison of SPEC with predictions.](image_url)

**Figure 2:** Specific purchased equipment costs (SPEC) of waste-heat recovery ORC systems and comparison with predictions. Data relating to commercial ORC systems are taken from Lemmens [43] and Quoilin et al. [78], both denoted by ‘x’. The data in Ref. [78] are presented in Euros (2013), whereas those in Ref. [43] are in Euros (2014); here, both are converted to GBP (2017) using the CEPCI values in Table B.3, with 2013 and 2014 average annual exchange rates of 0.849 £/€ and 0.806 £/€ respectively. Predictions obtained with in the present work with different approaches are all denoted by 'o'; (green) when using correlations from Turton [76], (red) when using corrections from Seider et al. [77], and (blue) when being determined by the combined costing methodology proposed here.

For smaller capacity/scale systems, with $\dot{W}_n < 30$ kW, the Turton [62] correlations seem to significantly overestimate the SPEC. This can be attributed to the costs of the two-phase sections of the heat exchangers. The correlation used for long-tube evaporators is valid in the range of 100 – 10,000 m$^2$, whereas the required areas for the two-phase sections as predicted by the model are typically in the range of 2 – 10 m$^2$. This illustrates a

---

1 The SPEC and the SIC are both metrics of costs divided by total power output of the system. However, the SPEC only accounts for the costs to purchase the equipment, whereas the SIC accounts for the total investment, thus including transportation and installation as well as equipment purchase costs.
general weakness of applying correlations to determine costs of equipment, which is that outside of a given capacity range, cost estimations may diverge from the actual costs and become increasingly inaccurate. At higher capacities, the Seider et al. [63] correlations seem to slightly underestimate the SPEC. Motivated by these observations, a mixed set of correlations where developed and applied in this study, which lead to SPEC values that agree reasonably well with the available cost data. The scatter of the commercial cost data arises from a multitude of factors, including differences in system construction, integration, sales volumes, profit margins, price uncertainty and many others. As only limited such data is available, this set is far from complete, and can only be used as rough guideline to validate the cost estimation methods.

The share of the various component costs is assessed here at different system scales. Figure 3 shows the relative ‘purchase equipment costs’ (PECs) of the heat exchangers, pump, expander and generator in a low-capacity (propane, $T_{\text{h.in}} = 150$ °C, $\dot{W}_n \approx 25$ kW) and a high-capacity ORC system (2-heptene, $T_{\text{h.in}} = 350$ °C, $\dot{W}_n \approx 150$ kW).

![Figure 3: Relative component costs for two different ORC systems. (a) Propane working fluid, $T_{\text{h.in}} = 150$ °C, $\dot{W}_n = 25.6$ kW, SIC = £10,120/kW. (b) 2-heptene working fluid, $T_{\text{h.in}} = 150$ °C, $\dot{W}_n = 150$ kW, SIC = £2,910/kW.](image)

Within the examined range, the contribution of the heat exchangers to the total system cost decreases with system size and heat-source temperature, whereas that of the turbine increases, in agreement with previous studies [43, 47,79–81]. This finding is further exemplified by a 2 kW system in Liege, Belgium, where 26% of the component costs were attributed to the expander and 62% of the costs were related to the heat exchangers [81]. Also, in a different 375 kW system, 60% of the total costs were attributed to the expander, pump and generator, while the condenser and evaporator accounted for only 22% and 13% of the total costs [43]. The breakdown predicted in this work, as presented in Fig. 3, matches the trends as observed for these systems while accounting for the variation in cost with system size; the trend that a smaller fraction of the costs is attributed to the heat exchangers, while the relative expander costs increase significantly, is correctly predicted. Thus, the current model provides reasonable estimates for the SIC of small- and medium-scale ORC systems with capacities between 20 and 200 kW, and is therefore suitable for a comparison between such systems.
2.5 Optimization procedure

Since the aforementioned SAFT-CAMD ORC model is non-linear and requires the specification of both integer and continuous decision variables, the optimization problem is classified as an MINLP problem. If the working fluid is pre-specified, only continuous system parameters need to be optimized and the optimization problem reduces to an NLP problem. The optimizations are carried out using a MATLAB implementation of the stochastic ‘non-dominating genetic algorithm II’ (NSGA-II) solver [82] that is capable of solving problems with either single or multiple objectives. An important aspect of stochastic solvers are the parameters of the solver, such as the number of generations, the population size, the cross-over fraction of variables and mutation-fraction of variables. More information on these parameters and their effects can be found in Srinivas and Deb [83]. The parameters that have been used to solve the optimization problems in this study are presented in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>NLP</th>
<th>MINLP</th>
<th>Multi-objective</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max. generations</td>
<td>60</td>
<td>150</td>
<td>200</td>
</tr>
<tr>
<td>Population size</td>
<td>150</td>
<td>400</td>
<td>500</td>
</tr>
<tr>
<td>Mutation fraction</td>
<td>0.3</td>
<td>0.6</td>
<td>0.7</td>
</tr>
<tr>
<td>Cross-over fraction</td>
<td>0.7</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Mutation scale</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Shrink factor</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Cross-over ratio</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

The set of equations below represents the general formulation of the optimization problem:

\[
\begin{align*}
\min_{x,z} & \quad f(x,z), \\
\text{s.t.} & \quad h(x,z) = 0, \quad g(x,z) \leq 0, \\
& \quad x \in [x_{lo}, x_{up}] \subseteq \mathbb{R}^n, \quad z \in [z_{lo}, z_{up}] \subseteq \mathbb{N}^m.
\end{align*}
\]

(13)\hspace{1cm}(14)\hspace{1cm}(15)\hspace{1cm}(16)

Here, \(x\) is the set of \(n\) continuous system variables, representing continuous decision variables in the system model, as stated in Sections 2.1 to 2.4, and \(z\) is the set of \(m\) integer variables describing the quantity of each molecular group in the working fluid. Further, \(f\) is the vector of objective functions: (i) the SIC in single-objective problems, or (ii) the TIC and \(\dot{W}_n\) in multi-objective problems. The set of equalities \(h\) contains all equations related to the thermodynamic cycle, the GC methods, heat exchanger sizing and costing methodology as well as the well-known octet rule, which is used as molecular feasibility constraint [84]:

\[
\sum_k n_k (2 - v_k) - 2 = 0.
\]

(17)

Here, \(n_k\) denotes the integer amount of molecular group \(k\) present in a molecule, and \(v_k\) the valency of molecular group \(k\). The value of \(v_k\) equals the number of bonds a molecular group type must form to obtain
eight electrons in the valence shell of the carbon atom. This ensures no bonds remain unused within a molecule. Cyclic molecules lead to a violation of Eq. 17 and are not assessed here. Two other constraints ensure that only an even number of groups containing a double bond can be present, and that the number of \( =\text{CH}_2 \) groups is equal to or less than the number of \( =\text{CH}– \) groups. These rules prevent combinations between single and double bonds, as well as infeasible numbers of \( =\text{CH}_2 \) end-groups in new molecules, and are implemented in the present model as conditional statements (presented in pseudo-code):

\[
\begin{align*}
\text{if } \cos\left(\pi(n_{=\text{CH}_2} + n_{=\text{CH}–})\right) < 0, \quad \text{then } f = 10^6, \text{ else } f = \text{SIC}; \\
\text{if } n_{=\text{CH}_2} \geq n_{=\text{CH}–}, \quad \text{then } f = 10^6, \text{ else } f = \text{SIC}.
\end{align*}
\]  

Thus, when the number of \( =\text{CH}– \) and \( =\text{CH}_2 \) groups are uneven, leading to an infeasible molecule, Eq. 18 ensures the vector of the objective function \( f \) takes on a large value of \( 10^6 \), which makes this solution very poor and it is rejected by the solver. Equation 19 ensures in a similar way that there can only be a feasible number of \( =\text{CH}_2 \) groups in the final solution. The set of inequalities \( g \) contains the following inequalities:

\[
\begin{align*}
T_{h,\text{out}} - T_3 &\geq \Delta T^{lo}, \quad (20) \\
T_{h,x} - T_4 &\geq \Delta T^{lo}, \quad (22) \\
T_{h,\text{in}} - T_6 &\geq \Delta T^{lo}, \quad (24)
\end{align*}
\]

where \( \Delta T^{lo} \) is the minimum temperature difference. These inequalities ensure that the temperatures of the hot and cold streams do not cross in the heat exchangers. It is common to set a \( \Delta T^{lo} > 10 \degree \text{C} \), to ensure reasonable values of \( A_s \). However, when the costs, and thus areas \( A_s \), are indirectly part of the objective function, no minimum temperature difference is required, since the solving algorithm will make a trade-off between high performance and low costs by adjusting \( \Delta T^{lo} \). Thus, in this work, \( \Delta T^{lo} = 0 \degree \text{C} \).

The vectors \( x^{lo} \), \( x^{up} \), \( z^{lo} \) and \( z^{up} \) are lower (lo) and upper (up) bounds on \( x \) and \( z \), respectively, contain:

\[
\begin{align*}
P_r &\leq 0.85, \quad (26) \\
P_{1-9} &\geq 0.25 \text{ bar(a)}, \quad (27) \\
\Sigma_k n_k &\leq 10. \quad (28)
\end{align*}
\]

In the above inequalities, Eq. 26 is introduced to ensure that the cycle remains subcritical, with a maximum pressure up to \( 85\% \) of \( P_{cr} \). Eq. 27 sets a lower bound of 0.25 bar (absolute) to the pressure in the system, and Eq. 28 is an upper bound on the number of groups in the molecule, limiting the complexity of the problem.

### 2.6 Case studies

In order to extend the generalization of the results obtained by our SAFT-CAMD ORC framework and examine

---

\(^2\) Ethylene (\( \text{H}_2\text{C=CH}_2 \)) is excluded by this constraint since \( T_d \) for ethylene is only 9 \degree \text{C} [31], which is lower than the inlet temperature of the cooling water. Thus, it is only present in the system as a vapour or supercritical fluid, making it unsuitable as a working fluid. In cases where \( T_{c,in} \) is lower, ethylene should also be considered.
how different system specifications influence the problem, three waste-heat recovery case studies are investigated that are similar to the case studies considered in White et al. [50] and Oyewunmi et al. [85]. It is assumed that an intermediate fluid-loop is in place between the ORC system and the heat source, which is common in commercial systems since this decreases system sensitivity to changing heat-source conditions [78]. The heat source is taken to be a flow of Therminol 66 in all cases, supplied at 150 °C, 250 °C or 350 °C, for which accurate property predicting correlations have been determined [86]. The heat sink is cooling water entering the condenser at 15 °C. Both $\eta_{\text{pump}}$ and $\eta_{\text{turb}}$ are assumed to take values of 70%. The remaining specifications are listed in Table 2.

Table 2: Waste-heat recovery case study definitions with heat source and sink specifications.

<table>
<thead>
<tr>
<th></th>
<th>$T_{\text{in}}$ [°C]</th>
<th>$\dot{m}$ [kg/s]</th>
<th>$c_p$ [J/kg K]</th>
<th>$v$ [m/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat source (h)</td>
<td>150, 250, 350</td>
<td>2.1</td>
<td>2,000</td>
<td>2.0</td>
</tr>
<tr>
<td>Heat sink (c)</td>
<td>15</td>
<td>5</td>
<td>4,200</td>
<td>1.5</td>
</tr>
</tbody>
</table>

3 Results and Discussion

3.1 ORC system performance from NLP optimization

A set of NLP optimizations is performed for the three case studies specified in Table 2, with the objective of minimizing the SIC. The working fluid is chosen a priori, from four common hydrocarbon families: $n$-alkanes, 2-methylalkanes (isoalkanes), 1-alkenes and 2-alkenes, by varying the number of $-\text{CH}_2-$ groups in the working fluid molecule. The general molecular formula of each hydrocarbon family is presented in Table 3; in the MINLP problems presented in Section 3.4, an assessment of more complex molecules is possible.

Table 3: Four hydrocarbon families and their constituent molecular groups as used in the NLP study.

<table>
<thead>
<tr>
<th>S/N</th>
<th>Hydrocarbon family</th>
<th>General formula</th>
<th>Molecular groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$n$-alkanes</td>
<td>$\text{H}_3\text{C}-(\text{CH}_2)_n-\text{CH}_3$</td>
<td>$-\text{CH}_3$ and $-\text{CH}_2-$</td>
</tr>
<tr>
<td>II</td>
<td>isoalkanes</td>
<td>$(\text{H}_3\text{C})_2-\text{CH}-(\text{CH}_2)_n-\text{CH}_3$</td>
<td>$-\text{CH}_3$, $-\text{CH}_2-$ and $&gt;\text{CH}-$</td>
</tr>
<tr>
<td>III</td>
<td>1-alkenes</td>
<td>$\text{H}_3\text{C}-(\text{CH}_2)_n-\text{CH}=\text{CH}_2$</td>
<td>$-\text{CH}_3$, $-\text{CH}_2-$, $=\text{CH}-$ and $=\text{CH}_2$</td>
</tr>
<tr>
<td>IV</td>
<td>2-alkenes</td>
<td>$\text{H}_3\text{C}-(\text{CH}_2)_n-\text{CH}=\text{CH}-\text{CH}_3$</td>
<td>$-\text{CH}_3$, $-\text{CH}_2-$ and $=\text{CH}-$</td>
</tr>
</tbody>
</table>

The remaining decision variables are $T_1$, $P_r$, $\tau$, $\Delta T_x$, $v_{\text{evap}}$ and $v_{\text{cond}}$. Results are shown in Fig. 4 for each heat source and hydrocarbon family. Here, $\dot{W}_{\text{n}}$, SIC and TIC are plotted against the number of carbon atoms in the working fluid ($C_n$). On average, the NLP optimizations required 9,000 evaluations and 4.4 hours of computing time.
As expected and as can be seen in Fig. 4a-c, a substantial increase in $\dot{W}_n$ is observed with increasing $T_{h,in}$. The highest $\dot{W}_n$ values when minimizing the SIC are 27.7 kW, 94.3 kW and 157.0 kW, in order of ascending $T_{h,in}$. The corresponding SIC values are £10,120/kW, £4,040/kW and £2,910/kW. Thus, a decrease of the SIC values is observed as the heat-source temperature (and consequently the system size) increases. From Fig. 4d-f, it also

---

Figure 4: (a-c) $\dot{W}_n$, (d-f) optimal (minimum) SIC, and (g-i) TIC of waste-heat recovery ORC systems with minimized SIC as determined by NLP optimizations at different heat-source temperatures; see Table 2.
follows that, for each hydrocarbon family, the molecular size and weight of the optimal working fluid (leading to the lowest SIC) increases with $T_{h,in}$. Specifically, the optimal molecular sizes are $C_3/C_4$ for $T_{h,in} = 150 \, ^\circ C$, $C_4/C_5$ for $T_{h,in} = 250 \, ^\circ C$ and $C_7$ for $T_{h,in} = 350 \, ^\circ C$. Thus, lighter fluids are favoured for the low-temperature heat sources, while increasingly heavier fluids are chosen at higher temperatures. A discussion on how molecular size relates to net power generation at different $T_{h,in}$ is provided in Section 3.2.1. The best performing (with respect to SIC) ORC systems employ propane, 2-butene and 2-heptene as the working fluid in order of increasing $T_{h,in}$.

In White et al. [50], optimizations of similar case studies were performed, but with the objective of maximizing $\dot{W}_n$. While an increase in $\dot{W}_n$ with $T_{h,in}$ was also reported, the $\dot{W}_n$ values reported are, on average, 37% higher than the values in Fig. 4a-c. This is not surprising as the objective in White et al. [50] was to maximize the $\dot{W}_n$, and the effect of pressure drops on the performance was not accounted for, resulting in higher $\dot{W}_n$. The working fluids that resulted in the maximum $\dot{W}_n$ were propane, 2-pentene and 2-hexene, for $150 \, ^\circ C$, $250 \, ^\circ C$ and $350 \, ^\circ C$ heat sources, respectively [50], while the highest $\dot{W}_n$ values reported in Fig. 4a-c are achieved with $n$-butane, 2-pentene and 2-hexene. Thus, using the SIC as the objective function leads to a reduction in $\dot{W}_n$ (in comparison with maximizing $\dot{W}_n$), and in the low-temperature case, a different working fluid that achieves the highest $\dot{W}_n$.

The costs, and specifically the SPEC values, corresponding to the optimized systems in the earlier SAFT-CAMD study of White et al. [50] were determined in Ref. [47]. On average, the SPEC values reported in Ref. [47] are 49% higher than those obtained in this work, and the lowest SPEC values are achieved by isohexane, 2-pentene and 2-heptene for the $150 \, ^\circ C$, $250 \, ^\circ C$ and $350 \, ^\circ C$ heat-source, respectively [47]. Thus, for both the $150 \, ^\circ C$ and $250 \, ^\circ C$ cases, different working fluids (propane and 2-butene) are identified as having the lowest SPEC in this work. Since multiplying the SPEC with a multiplication factor results in the SIC, minimizing the SIC is expected to lead to similar optimal systems to optimizing the SPEC. From this comparison, it is clear that minimizing the SIC indeed results in less costly systems, but also in lower capacities. The SIC/SPEC and $\dot{W}_n$ are roughly inversely related, as higher values for $\dot{W}_n$ generally correspond to lower values of SIC.

The total investments costs, TIC, of each ORC system are shown in Fig. 4g-i. For the $250 \, ^\circ C$ and $350 \, ^\circ C$ heat sources, the highest TIC is required by systems employing $C_5$ and $C_6$ working fluids. For a $T_{h,in}$ of $150 \, ^\circ C$, the molecular size that achieves the highest TIC varies between the hydrocarbon families. Between the lowest and highest heat-source temperature, an increase in the maximum TIC from £288,000 to £466,100 is observed. Thus, both the TIC and $\dot{W}_n$ increase with heat source temperature. However, the highest TIC increases by a factor of roughly 1.6, whereas the highest $\dot{W}_n$ increases by a factor of 6. This illustrates how the total costs of an ORC system increase with the capacity of the system, while the costs per kW (the SIC) decreases.

Thus, from these results, it appears that the SIC represents a useful techno-economic parameter to describe the trade-off between performance and cost. For example, for a 150 °C heat-source temperature, ORC systems with $C_3$ working fluids (1-propene or propane) have lower SICs than their respective $C_4$ alternatives (1-butene and $n$-butane). However, systems with 1-butene and $n$-butane achieve higher $\dot{W}_n$ than those with 1-propene and propane.

---

3 In Ref. [47], the ratio of purchased equipment costs divided by power output was reported. This metric is equal to the SPEC, as mentioned in Section 2.4.
This is a direct illustration of how minimizing the SIC leads to choosing a working fluid that can achieve a high $\dot{W}_n$ at low cost, and how merely choosing a system that maximizes $\dot{W}_n$ can lead to a suboptimal SIC.

To compare the TIC component breakdown for different heat sources and working fluids, the bare module costs are shown in Fig. 5. For each heat source, these costs are only shown for the hydrocarbon family containing the optimal working fluid (minimum SIC), thus, the $n$-alkanes are shown in Fig. 5a and 2-alkenes are shown in Fig. 5b and 5c. In Fig. 4g, an increase in the TIC is observed between systems with propane and $n$-butane. From Fig. 5a, it follows that this rise in the TIC can solely be attributed to an increase in the evaporator costs. Furthermore, a slight decrease in TIC is observed between systems with $n$-butane and $n$-hexane in Fig. 4g. Between these fluids, $\dot{W}_n$ decreases, and this translates directly to a decrease in turbine costs, as can be seen in Fig. 5a.

![Figure 5](image_url)

Figure 5: Bare module costs of waste-heat recovery ORC systems with SICs optimized at different heat-source temperatures. I and IV refer to the $n$-alkane (I) and 2-alkene (IV) hydrocarbon families; see Table 3. Since there is no $C_3$ 2-alkene in Fig. 4, the minimum number of carbon atoms shown in Fig. 5b and 5c is $C_4$.

On average, the two heat exchangers account for 74% of total bare module costs in the 150 °C heat-source case study, but this fraction decreases to 50% and 39% for the 250 °C and 350 °C heat sources, respectively. The turbine accounts for 17%, 40% and 52% of the costs, in order of increasing $T_{\text{in}}$, as the costs of the turbine are directly related to $\dot{W}_n$. Another general trend, which applies to all three heat sources, is an increase in the evaporator and decrease in the condenser costs, when comparing the lightest and heaviest working fluids.

### 3.2 Effect of decision variables on optimal design

#### 3.2.1 Molecular size of the working fluids

The molecular size of the working fluid has a significant effect on both the thermodynamic performance and the cost of ORC systems. The critical properties are related to the molecular size, since an increase in the
number of carbon atoms tends to increase $T_c$ and decrease $P_c$. Thus, at any fixed subcritical pressure, a larger and heavier hydrocarbon will have a higher saturation temperature. Conversely, this also means that at a fixed evaporation temperature, the corresponding pressure will be higher when using smaller/lighter hydrocarbons.

The pressure ratio associated with the expansion across the turbine increases by either increasing $P_{evap}$ or decreasing $P_{cond}$, which results in a larger $W_{turb}$ and $W_n$. The temperature of the working fluid in both heat exchangers is limited by the temperature of the heat source and sink. Throughout the length of the evaporator, the working fluid temperature cannot exceed the temperature of the heat source, and throughout the condenser, the temperature of the working fluid cannot go below the temperature of the cooling water. Therefore, $P_{evap}$ and $P_{cond}$ are indirectly limited by the corresponding saturation temperatures, which have to satisfy these constraints at any arbitrary point in the heat exchangers. Furthermore, $P_r$, and thus $P_{evap}$, is bound by $P_{cr}$. The operating pressures for the best performing hydrocarbons at each $T_{h,in}$ are presented in Fig. 6, where it can be seen that $P_{evap}$ and $P_{cond}$ decrease as the molecular size of the working fluid increases. This is in agreement with the observation that fluids with larger molecular sizes have lower $P_c$ and higher $T_c$. For the 150 °C heat source, only a system with propane can operate at a pressure of 85% of $P_c$ without the working fluid exceeding the temperature of the heat source. At heat-source temperatures of 250 °C and 350 °C, working fluids can reach higher temperatures in the evaporator. This results in an increasing amount of working fluids for which $P_{evap}$ is not bound by the heat source temperature in the evaporator, but by the upper pressure bound. For the 350 °C heat source, only the systems with C$_9$ working fluids have a $P_r$ that is lower than 85% of $P_c$.

When the molecular size increases, the saturation pressure related to a given temperature decreases, which applies also to the condensation process. In the condenser, the cooling water enters at a temperature of 15 °C in all cases, and the condensation temperature remains roughly constant. Hence, $P_{cond}$ will be lower for heavier working fluids, without violating the constraint that the working fluid temperature cannot drop below
the cooling water temperature at any point in the heat exchanger, which explains the observed decrease in $P_{\text{cond}}$ with increasing molecular size; in effect, $P_{\text{cond}}$ is strongly determined by the chosen value of the decision variable $T_1$. Thus, the molecular size of a fluid that achieves a high $W_n$ at any $T_{\text{h,in}}$ ensures a high pressure in the evaporator and a low pressure in the condenser, resulting in a large pressure ratio. Since SIC is inversely proportional to $W_n$, molecular size directly influences SIC.

3.2.2 Temperature differences in the heat exchangers

In Fig. 7, $\Delta T_{\text{pinch}}$, which is the smallest temperature difference between the working fluid and heat source/sink streams in the heat exchangers is shown in both the evaporator and condenser. The temperature difference generally increases with $T_{\text{h,in}}$, and also in the condenser it increases with the molecular size of the working fluid.

![Graph showing temperature differences](image)

Figure 7: Minimum temperature difference between the working fluid and the heat source (evaporator) or cooling water (condenser) in systems for which SIC is optimized. I and IV refer to the $n$-alkane (I) and 2-alkene (IV) hydrocarbon families; see Table 3.

For the 150 °C heat source case, $\Delta T_{\text{pinch}}$ does not drop below 8 °C for systems with $n$-butane, $n$-pentane and $n$-hexane. However, for these working fluids, $P_t$ is lower than 0.85 so that no constraint is active. In the case of the 350 °C heat source, $P_t$ reaches the constraint value of 0.85 for most fluids. Nevertheless, $\Delta T_{\text{pinch}}$ can be chosen independently and is not directly related to the value of $P_t$. If $\Delta T_{\text{pinch}}$ becomes smaller, this leads to an increase in $\dot{m}_{\text{ref}}$ and more heat being transferred from the heat source to the working fluid. For all NLP optimized systems, $\Delta T_t$ is the smallest temperature difference achieved in the evaporator. Thus, $\Delta T_t$ and $\Delta T_{\text{pinch}}$ coincide in all optimized systems. To demonstrate the effect slight changes in $\Delta T_t$ have on the system, a sensitivity analysis is performed for the optimized system with 2-heptene and a heat source temperature of 350 °C. The results from this analysis are presented in Fig. 8.
Figure 8: Influence of: (a) $\Delta T_x$ on $A_{s,ev}$ and $\dot{W}_n$, and (b) $\Delta T_x$ on SIC for an ORC system optimized with a 350 °C heat source and 2-heptene as the working fluid, which attained the minimum SIC for this case; see Fig. 2.

From Fig. 8a, it follows that an increase in $\Delta T_x$ has two effects on the system. The area $A_{s,ev}$ decreases, which reduces the heat exchanger size and cost, as well as the overall system cost. However, $\dot{W}_n$ decreases as well. Similarly, decreasing $\Delta T_x$ leads to higher $A_{s,ev}$ and $\dot{W}_n$. In Fig. 8b, the corresponding SIC is shown. The lowest value is achieved at $\Delta T_x = 45.6$ °C, which is also the value identified during optimization.

The discontinuities are a reflection of the available costing techniques. In order to avoid impractical solutions, a maximum area is set for the single-phase double-pipe heat exchangers of 10 m$^2$ [76]. If $A_s$ exceeds this limit, a second heat exchanger needs to be purchased. If this is only a small heat exchanger, the costs per m$^2$ are relatively high. With increasing $A_s$, the surface specific cost decrease, resulting in a SIC decrease between the discontinuities in Fig. 8b. This demonstrates how this specific $\Delta T_x$ is chosen as a trade-off between a high $\dot{W}_n$, and a moderate $A_{s,ev}$ (and costs).

3.2.3 Velocities in the heat exchangers and superheating

The influence of $v_{cond}$ and $v_{evap}$ on $A_s$ and $\dot{W}_n$ is illustrated for a system with $n$-pentane as working fluid in Fig. 9. This system is optimized for a minimum SIC. The solutions of the NLP problems contain substantially lower values of $v_{cond}$, as a result of the effect of the pressure drops on the performance of the pump and the turbine. The properties of the liquid are less sensitive to pressure changes and $\Delta P_{evap}$ has a less pronounced effect on the performance of the cycle. Therefore, the optimal operating conditions that are chosen lead to a $\Delta P_{cond}$ that is significantly lower than $\Delta P_{evap}$, and $\dot{W}_n$ is more sensitive to the value of $v_{cond}$ than the value of $v_{evap}$.

The discontinuity observed in Fig. 9b is caused by transitions between different condensing flow regimes and the corresponding correlations for predicting the heat transfer coefficients $\alpha$, as described in Section 2.3. By varying $v_{cond}$, subsections of the two-phase section of the condenser transition to different flow regimes, causing a sudden change in heat exchanger length, and $\Delta P_{cond}$. In real systems, these discontinuities are not expected to occur with smooth transitions appearing instead, highlighting a limitation of using such empirical correlations.
Figure 9: Influence of: (a) $v_{\text{ev}}$ on $A_{\text{ev}}$ and $W_n$, and (b) $v_{\text{cond}}$ on $A_{\text{cond}}$ and $W_n$ for an ORC system optimized with a 150 °C heat source and n-pentane—a common candidate in ORC system installations [20]—as the working fluid.

As stated in Section 2.1, $z$ is a dimensionless variable that indicates the amount of superheating that occurs in the evaporator. The values of $z$ for all working fluids and heat-source temperatures are shown in Fig. 10. For each $T_{h,in}$, the optimal cycle is seen to feature less superheating for larger and heavier molecules, such that no superheating ($z = 0$) is required for the heaviest molecules. This is due to the fact that the heavier fluids become drier (i.e., they have a positively sloping dew-point curve on the $T$-$s$ diagram), and as such, superheating leads to detrimental effects on the cycle performance [44,87], in this case leading to higher SIC values.

As can also be seen in Fig. 10, substantial superheating occurs with lighter hydrocarbon working fluids. As $T_{h,in}$ increases, more superheating is required for heavier hydrocarbons. The evaporating pressure of light hydrocarbons is limited by the upper bound on $P$. This leads to a limitation on the evaporating temperature as well, and therefore the amount of heat that can be transferred from the heat source to the working fluid in the preheating section of the evaporator. In such cases, additional superheating can lead to the transfer of more heat to the system, and therefore an increase the power output $W_n$ from the system.

Figure 10: Values of normalized degree of superheating ($z$) for systems optimized with SIC as the objective function.
3.3 Choice of objective function

All optimization results presented above were generated when the objective was to minimize the SIC. In order to consider the significance of the choice of the objective function, two additional optimizations were performed for an ORC system with $T_{h,in} = 350 \degree C$ and 2-heptene, i.e., the combination of heat-source temperature and working fluid that yielded the lowest overall SIC value in Fig. 4. In the both additional instances, the objective was to maximize $\dot{W}_n$ (i.e., $f$ in Eq. 13 is max{$\dot{W}_n$} instead of either min{SIC}), and in one of the optimizations where $\dot{W}_n$ was maximized, minimum $\Delta T_{\text{pinch}}$ constraints of 10 °C in the evaporator and condenser were imposed (i.e., $\Delta T_{\text{bo}} = 10 \degree C$ in Eqs. 20-25). The results are presented in Table 4.

<table>
<thead>
<tr>
<th>Objective function</th>
<th>$\Delta T_{\text{bo}}$ [°C]</th>
<th>SIC [£/kW]</th>
<th>$\dot{W}_n$ [kW]</th>
<th>TIC [£]</th>
<th>$T_{h,\text{out}}$ [°C]</th>
<th>$A_{s,\text{ev}} + A_{s,\text{co}}$ [m²]</th>
<th>$\Delta T_{\text{pinch,ev}}$ [°C]</th>
<th>$\Delta T_{\text{pinch,co}}$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min. SIC</td>
<td>0</td>
<td>£2,910</td>
<td>150.8</td>
<td>£438,370</td>
<td>115.8</td>
<td>40</td>
<td>41.8</td>
<td>34</td>
</tr>
<tr>
<td>Max. $\dot{W}_n$</td>
<td>0</td>
<td>£4,560</td>
<td>221.2</td>
<td>£1,008,020</td>
<td>58.3</td>
<td>1,709</td>
<td>0.1</td>
<td>13</td>
</tr>
<tr>
<td>Max. $\dot{W}_n$</td>
<td>10</td>
<td>£4,320</td>
<td>210.3</td>
<td>£908,380</td>
<td>70.0</td>
<td>541</td>
<td>10.1</td>
<td>15</td>
</tr>
</tbody>
</table>

The choice of the objective function has a significant effect on the optimal solution. When maximizing $\dot{W}_n$, the system costs are neglected, which has numerous effects on the optimal operating conditions. As can be seen in Fig. 9, decreasing $\nu$ leads to an increase of both $\dot{W}_n$ and $A_s$. Since the heat-exchanger costs are not part of the objective, low flow velocities are identified as optimal, leading to small pressure drops and a $\Delta T_{\text{bo}}$ of only 0.1 °C. The heat-source temperature shows the largest decrease for this objective. This makes intuitive sense as it corresponds to the highest heat transfer rate from the heat source to the working fluid undergoing the cycle, and hence the possibility to generate more power. However, the small $\Delta T_{\text{pinch}}$ leads to large $A_s$. When a constraint of $\Delta T_{\text{bo}} = 10 \degree C$ is imposed, the total $A_s$ decreases significantly, limiting $\dot{W}_n$ but also substantially reducing the TIC. From this comparison it can be concluded that using the SIC as the objective function enables the solving algorithm to make trade-offs between costs and performance. Maximizing $\dot{W}_n$, on the other hand, requires the introduction of additional constraints, which are not necessary when using the SIC as objective, in order to prevent the identification of solutions with excessive $A_s$ and/or TIC values. Furthermore, lower bounds on $\nu$ should be specified, again to prevent excessive $A_s$, and the transition to different flow regimes within which the correlations used for predicting $\alpha$ and $\Delta P_t$ are less reliable.

3.4 Optimal working-fluid and ORC system designs via MINLP formulations

In all preceding sections, working fluid classes were specified manually prior to optimization. Although this allows a systematic comparison of different hydrocarbons, it is not an effective strategy to screen a large
number of fluids or to find novel (or new) fluid candidates. In order to overcome these limitations and to prevent the use of heuristic-based preselection, working fluids are incorporated into the optimization decision space as a collection of integer variables, indicating the quantity of each molecular group in the working fluid. More complex formulations are possible in these MINLP problems.

In this problem formulation, the molecular feasibility constraints enumerated in Section 2.5 (Eqs. 17 to 19) ensure that infeasible molecular combinations are not arrived at, making the problem more tractable. Without the molecular feasibility constraints, the six molecular groups employed in this study can be combined in roughly 1.8 million ways. However, only 128 combinations satisfy all molecular feasibility constraints, and thus are feasible molecules. The complete set of \( n \)-alkanes, isoalkanes, 1-alkenes and 2-alkenes only contains 27 working fluids that contain 10 or less molecular groups. Thus, only a small subset of all possible working fluids is assessed when only common hydrocarbon families are considered.

In this section, the results of two waste-heat recovery case studies with \( T_{\text{h,in}} \) of 150 °C and 250 °C are presented. All other specifications are similar to those used earlier and presented in Table 2. In this exercise, the working fluid that was identified as optimal after each run was then excluded from the decision space of subsequent runs, by adding an additional constraint called an integer cut that penalizes future occurrence of that solution and prevents the solver from converging on the same working fluid twice.

The results of eight consecutive MINLP optimizations are shown in Table 5 for \( T_{\text{h,in}} = 150 \) °C and Table 6 for \( T_{\text{h,in}} = 250 \) °C. In Table 5 (\( T_{\text{h,in}} = 150 \) °C), the best performing working fluid is 1,3-butadiene and the remaining fluids are all members of the hydrocarbon families identified in the NLP optimizations. On the other hand, in Table 6 (\( T_{\text{h,in}} = 250 \) °C), only 2-butene and 2-pentene are members of these hydrocarbon families. Thus, the MINLP solver was able to identify novel working fluids that have not been assessed previously by traditional NLP methods. Furthermore, the ORC systems with the two best ranked molecules in Table 6 have a substantially lower SIC. This can be attributed to the slight overestimation of the \( P_{\text{cr}} \) value predicted by the empirical GC method compared to the value that is inherently determined through SAFT-\( \gamma \) Mie. Only subcritical ORC systems are examined in this study, and an upper bound on \( P_r \) of 0.85 is introduced to prevent critical or supercritical evaporating conditions. For these working fluids, the value of \( P_{\text{evap}} \) that is limited at 0.85 \( P_{\text{cr}} \) (from the empirical GC correlations), is very close to the \( P_{\text{cr}} \) that follows from SAFT-\( \gamma \) Mie. At such pressures, the enthalpy of evaporation becomes negligible, since the saturated liquid and vapour lines are very close or even coincide and, therefore, the \( A_s \) of the two-phase sections becomes almost negligible as well, leading to low TIC and SIC values.

In Appendix C, the \( T-s \) diagrams and key thermodynamic properties of the working fluids identified through the MINLP optimization are shown. Only the novel working fluids are shown; common working fluids with accessible properties from databases such as REFPROP and COOLPROP are excluded. Most of working fluids have very similar \( T-s \) diagrams and can be classified as dry working fluids. The results presented in these tables are valuable for the design of ORC systems. Through the sequential MINLP optimizations and integer cuts, a
selection of potentially suitable working fluids and operating conditions can be found relatively easily using the proposed framework; the final choice of the working fluid can then be based on the cost and/or availability of the working fluid or at the discretion of the design engineer. During the detailed design phases in ORC installation project, these solutions could be further investigated to determine the final working fluid and system design.

Table 5: MINLP results with \( T_{h,in} = 150 \) °C. Ranking is based on the value of the objective function (SIC), and finding order refers to the order in which the working fluids were identified as optimal solutions by the solver.

<table>
<thead>
<tr>
<th>Rank</th>
<th>Finding order</th>
<th>Molecular groups</th>
<th>Systematic name</th>
<th>SIC [£/kW]</th>
<th>( \dot{W}_n ) [kW]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7</td>
<td>H(_2)C=CH–CH=CH(_2)</td>
<td>1,3-butadiene</td>
<td>£9,645</td>
<td>26.7</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>H(_3)C–CH(_2)–CH(_3)</td>
<td>propane</td>
<td>£10,106</td>
<td>25.3</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>(H(_2)C)(_2)–CH–CH(_3)</td>
<td>isobutane</td>
<td>£10,142</td>
<td>27.6</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>H(_3)C–CH=CH(_2)</td>
<td>propene</td>
<td>£10,277</td>
<td>24.6</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>H(_3)C–CH(_2)–CH=CH(_2)</td>
<td>1-butene</td>
<td>£10,369</td>
<td>27.9</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>H(_3)C– (CH(_2))(_2)–CH(_3)</td>
<td>( n )-butane</td>
<td>£10,406</td>
<td>27.7</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>H(_3)C–CH=CH–CH(_3)</td>
<td>2-butene</td>
<td>£10,418</td>
<td>26.0</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>H(_3)C– (CH(_2))(_3)–CH(_3)</td>
<td>( n )-pentane</td>
<td>£11,080</td>
<td>25.6</td>
</tr>
</tbody>
</table>

Table 6: MINLP results with \( T_{h,in} = 250 \) °C. Ranking is based on the value of the objective function (SIC), and finding order refers to the order in which the working fluids were identified as optimal solutions by the solver.

<table>
<thead>
<tr>
<th>Rank</th>
<th>Finding order</th>
<th>Molecular groups</th>
<th>Systematic name</th>
<th>SIC [£/kW]</th>
<th>( \dot{W}_n ) [kW]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>(H(_3)C)(_3)–C–CH=CH–CH(_3)</td>
<td>4,4-dimethyl-2-pentene</td>
<td>£3,569</td>
<td>82.4</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>(H(_2)C)(_2)–C– (CH(_2))(_2)</td>
<td>3,3-dimethyl-1,4-pentadiene</td>
<td>£3,603</td>
<td>78.6</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>(H(_2)C)(_2)–CH–CH=CH–CH(_3)</td>
<td>4-methyl-2-pentene</td>
<td>£4,001</td>
<td>91.5</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>H(_3)C–CH=CH–CH(_3)</td>
<td>2-butene</td>
<td>£4,019</td>
<td>88.6</td>
</tr>
<tr>
<td>5</td>
<td>8</td>
<td>(H(_3)C)(_3)–C–CH(_2)–CH(_3)</td>
<td>2,2-dimethylbutane</td>
<td>£4,110</td>
<td>83.9</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>H(_3)C–CH– (CH(_2))(_2)</td>
<td>3-methyl-1,4-pentadiene</td>
<td>£4,121</td>
<td>90.8</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>H(_3)C–CH=CH–CH(_2)–CH(_3)</td>
<td>2-pentene</td>
<td>£4,124</td>
<td>96.0</td>
</tr>
<tr>
<td>8</td>
<td>7</td>
<td>H(_3)C=CH–CH(_2)–CH=CH(_2)</td>
<td>1,4-pentadiene</td>
<td>£4,223</td>
<td>95.0</td>
</tr>
</tbody>
</table>

3.5 ORC system design via multi-objective problem formulations

As discussed in Section 3.1, an inherent trade-off between the TIC and \( \dot{W}_n \) is made when performing optimizations with the SIC as objective function. A multi-objective optimization can be performed to obtain more insight into the relation between these two objectives. For these optimizations, the vector \( \mathbf{f} \) in Eq. 13
contains both TIC and $\dot{W}_n$. Using the NSGA-II solver, both the TIC and $\dot{W}_n$ can be optimized simultaneously, obtaining a set of ‘non-dominated Pareto-front’ solutions. For each of these solutions, it is not possible to obtain a better value for one of the objectives without degrading the other objectives. The algorithm regards the set of solutions within a Pareto-front as equally optimal, or non-dominated. From this set, a final solution can be chosen, while taking the relative importance of each objective into consideration.

To compare the results obtained from the multi-objective optimization with the MINLP results, the $T_{h,in} = 250 ^\circ$C case study is used. Two distinct optimizations have been performed. First, to demonstrate the suitability of the NSGA-II solver for multi-objective MINLP problems, only the 2-alkenes were considered during the optimization. Thus the only integer decision variable was the number of –CH$_2$– groups present in the 2-alkene, with general formula $\text{H}_3\text{C}-(\text{CH}_2)_n-\text{CH}=$CH–CH$_3$. In a second optimization, all molecular groups were considered as decision variables, and both 4,4-dimethyl-2-pentene and 3,3-dimethyl-1,4-pentadiene (where the deviation in $P_{cr}$ values was excessive) are excluded from the search space. On average, the multi-objective optimizations required 100,000 evaluations taking 25.4 hours of computing time.

The results of the first optimization exercise are presented in Fig. 11. Of all 2-alkenes, the best SIC value is obtained with 2-butene, which is in agreement with the results shown in Fig. 4e. From Fig. 11, it follows that at system capacities of 85 kW or higher, 2-pentene is preferred over 2-butene. Thus, if a capacity exceeding 85 kW is required, 2-pentene might be a better working fluid than 2-butene since it requires a lower SIC at these capacities. This illustrates how a multi-objective optimization can provide additional insight into the optimal solutions over a range of system characteristics. If only a single objective optimization is applied, no information about the behaviour of sub-optimal systems is obtained.

![Figure 11](image-url): Results of multi-objective optimization for 2-alkenes with $T_{h,in} = 250 ^\circ$C.
Figure 12: Results of multi-objective optimization with $T_{hi} = 250$ °C (4,4-dimethyl-2-pentene and 3,3-dimethyl-1,4-pentadiene are excluded from the search space). (a) TIC against $\dot{W}_n$. (b) Three-dimensional TIC, $\dot{W}_n$ and SIC plot. The grey points are projections of the data points on the SIC-$\dot{W}_n$ and SIC-TIC planes.

The results of the second optimization exercise are presented in Fig. 12. As expected, the excluded fluids do not appear in the Pareto-front shown in Fig. 12a. The working fluid that yields the best SIC is 4-dimethyl-2-pentene, which is also the best working fluid identified in the MINLP optimization after the exclusion of 4,4-dimethyl-2-pentene and 3,3-dimethyl-1,4-pentadiene. The reported trade-off between $\dot{W}_n$ and TIC can be seen in Fig. 12b, since systems which achieve a high $\dot{W}_n$ also lead to a high TIC. In the same vein, systems requiring a low investment also have a high SIC. Finally, within the power output range from 60 kW to 110 kW, SIC values between £4,000/kW and £4,200/kW can be achieved. This can be observed in the two-dimensional projection of the Pareto-front on the SIC-$\dot{W}_n$ plane. Within this capacity range, the SIC value is not sensitive to $\dot{W}_n$, and remains roughly constant. Thus, this multi-objective optimization allows the designer to select a desired power output from a range of capacities and still achieve a SIC which is close to the optimum value.

Finally, the outputs from the multi-objective MINLP optimization are compared with the data from actual ORC implementations and these results are shown in Fig. 13, in which the SPEC values associated with the solution-front is compared to the SPEC values obtained from Refs. [43] and [78].

For a more detailed and accurate comparison, more information on real-world ORC applications is required, e.g., the heat source temperature and cycle configuration(s) of interest. However, from Fig. 13, it can be concluded that the solutions obtained during the optimization seem to outperform the actual ORC system implementations. The minimum SPEC is found at approximately 90 kW, but at all evaluated capacities the proposed solutions result in lower SPEC values than the actual ORC implementations. At capacities greater than 100 kW, the SPEC difference between the solutions and real-world applications diminishes. Thus, for a specific capacity range, the framework enables a sufficient and effective way to optimize ORC systems and working fluids, thereby validating the proposed optimization procedure.
Figure 13: Specific purchased equipment costs (SPECs) of ORC waste-heat recovery systems, taken from Refs. [43] and [78], and results of multi-objective optimization with \( T_{h,m} = 250 \, ^\circ C \) (4,4-dimethyl-2-pentene and 3,3-dimethyl-1,4-pentadiene are excluded from the search space). The data in Ref [78] is presented in Euros (2013) while that in Ref [43] is in Euros (2014); they are converted to GBP (2017) using the CEPCI values from Table B.3, with the 2013 and 2014 average annual exchange rates of 0.849 £/€ and 0.806 £/€ respectively.

4 Conclusions

Traditionally, working fluids for organic Rankine cycle (ORC) systems have been selected via heuristic approaches and the (pre-)screening of known substances. However, computer-aided molecular design (CAMD) methods allow the design of an optimal working fluid during ORC system optimization in specific cases, enabling the possible identification of novel, previously-unavailable working fluids. In this paper, a thermo-economic CAMD-ORC framework is developed and applied to subcritical and non-recuperated ORC systems in waste-heat recovery applications represented by a range of heat-source temperatures from 150 °C to 350 °C. The framework returns, in addition to the optimal working fluid, the optimal design variables (cycle pressures, temperatures and heat exchanger fluid velocities) of the ORC system.

While there is a relation between high net power output \( \dot{W}_n \) and low specific investment cost (SIC), minimizing the SIC and maximizing \( \dot{W}_n \) are not directly equivalent objectives and therefore do not lead to the same results. Merely maximizing the \( \dot{W}_n \) and/or minimizing the total investment cost (TIC) result in costly or poor performing systems. Introducing a pinch point constraint is necessary when maximizing \( \dot{W}_n \), in order to prevent the identification of systems with excessive heat exchange surface areas and costs. However, when the SIC is minimized, such pinch point constraints are not necessary as the nature of the objective requires the solver to strike a balance between the ORC system performance (which is favoured by very low pinch point constraints) and the system costs that are minimized by large temperature differences between the heat sources.
source/sink and the working fluid in the heat exchangers. Furthermore, the molecular size of the optimal working fluids is related to the heat-source temperature, with heavier and more complex fluids that have higher critical temperatures being optimal at higher temperatures.

The presently proposed framework can effectively identify novel working-fluid candidates via mixed-integer non-linear programming (MINLP) optimization. Eight consecutive MINLP optimizations with the minimum SIC as objective were performed for ORC systems with heat source temperatures of 150 °C and 250 °C. In both cases, novel working fluids that do not belong to the common hydrocarbon families assessed in the NLP optimizations are identified. In addition, of the five working fluids present from a multi-objective Pareto-front of optimal solutions, three are identified during the single-objective MINLP optimizations. These sets of NLP, MINLP and multi-objective MINLP optimizations have proven that the current framework is capable of designing optimal ORC systems for a variety of heat-source temperatures and capacities, and is also capable of deriving suitable optimal working-fluid(s) for each system while doing so.

Of further interest are the incorporation of additional molecular groups and molecular constraints into the problem formulations. This would allow the assessment of a larger family of working fluids, such as aromatics, alcohols or ethers. Decision variables for cycle architectures can also be directly incorporated in the decision space to enable the design of transcritical or recuperated cycles, or cycles with working-fluid mixtures, etc. It is also important to consider a variety of economic metrics such as the net present value, levelized cost of electricity or the operational costs and revenue, potentially forming a better basis for comparison between systems and enabling a more informed decision on the economic prospects of ORC systems in general.

**Acknowledgment**

This work was supported by the UK Engineering and Physical Sciences Research Council (EPSRC) [grant number EP/P004709/1]. Data supporting this publication can be obtained on request from cep-lab@imperial.ac.uk.

**Appendix A: Heat transfer coefficient determination**

The correlations used in this work for single and two-phase heat transfer are presented in this appendix. In particular, the Dittus-Boelter (subscript ‘DB’) equation was used for single-phase heat transfer [66],

\[ \alpha_{DB} = \frac{\lambda}{D_{hyd}} 0.023 Re^{0.8} Pr^n, \]  

(A.1)

where \( \alpha_{DB} \) denotes the Dittus-Boelter heat transfer coefficient, \( D_{hyd} \) the hydraulic diameter and \( Pr \) the dimensionless Prandtl number; \( n \) takes the value 0.3 for fluids being cooled, and 0.4 for fluids being heated.

Furthermore, distinct Reynold numbers were used in the two-phase heat transfer correlations:

\[ Re_L = \frac{\rho_L \nu_{wef} (1-x)}{\mu_L} \]  

(A.2)
The asymptotic correlation by Dobson (subscript ‘Dob’), Steiner and Taborek [65] and Liu and Winterton [69] were employed. The correlation developed by Chen [67] is given by the following set of equations:

\[ \alpha_{\text{Chen}} = \alpha_{\text{DBL}} F_{\text{Chen}} + \alpha_{\text{NB}} S_{\text{Chen}}, \]

\[ \alpha_{\text{DBL}} = 0.023 \frac{\lambda}{\mu} (ReL)^{0.8} Pr_{L}^{0.4}, \]

\[ \alpha_{\text{NB}} = 0.00122 \left( \frac{\lambda_{L}^{0.89}}{\rho_{L}^{0.45} \mu_{L}^{0.44}} \right) \Delta T_{\text{sat}}^{0.24} \Delta P_{\text{sat}}^{0.75}, \]

\[ \Delta T_{\text{sat}} = T_{\text{wall}} - T_{\text{sat}}, \]

\[ \Delta P_{\text{sat}} = P \left\{ \exp \left( \frac{h_{LV} \text{MW}}{R} \frac{1}{T_{\text{sat}}} - \frac{1}{T_{\text{wall}}} \right) - 1 \right\}, \]

\[ F_{\text{Chen}} = \begin{cases} 1.0 & \text{if } \frac{1}{X_{tt}} \leq 0.1, \\ 2.35 \left( \frac{1}{X_{tt}} + 0.213 \right)^{0.736} & \text{if } \frac{1}{X_{tt}} > 0.1, \end{cases} \]

\[ \frac{1}{X_{tt}} = \left( \frac{x}{1-x} \right)^{0.9} \left( \frac{\rho_{L}}{\rho_{v}} \right)^{0.5} \left( \frac{\mu_{v}}{\mu_{L}} \right)^{0.1}, \]

\[ \frac{1}{S_{\text{Chen}}} = 1 + 2.53 \times 10^{-6} \left( ReL \right)^{1.25} F_{\text{Chen}}^{1.17}, \]

where \( \alpha_{\text{NB}} \) is the nucleate boiling heat transfer coefficient (subscript ‘NB’), \( h_{LV} \) is the specific enthalpy of evaporation, \( T_{\text{wall}} \) the inner wall temperature, \( T_{\text{sat}} \) the saturation temperature at the evaluated pressure, MW the molar weight of the working fluid, \( R \) the universal gas constant, \( x \) the vapour quality, \( X_{tt} \) the Lockhart-Martinelli parameter, and finally, \( S_{\text{Chen}} \) and \( F_{\text{Chen}} \) are multiplication factors used for the forced convection and nucleate boiling contributions to overall heat transfer, respectively.

The asymptotic correlation proposed by Dobson (subscript ‘Dob’) is as follows:

\[ \alpha_{\text{Dob}} = \frac{N_{\text{Dob}} \lambda_{L}}{D_{\text{in}}}, \]

\[ N_{\text{Dob}} = \left( N_{\text{Watt}}^{2.5} + N_{\text{Coop}}^{2.5} \right)^{0.5}, \]
\[ N_{u,Watt} = 0.023 \, F_{Watt}(R_e)_L^{0.8} \, P_r_L^{0.4} \, \left( 1 + \frac{1.925}{x_{te}^{0.685}} \right), \]  
\[ F_{r_L} = \frac{g^2}{\rho L D_{in}^2}, \]  
\[ F_{Watt} = \begin{cases} 1.0 & \text{if } F_{r_L} \geq 0.25, \\ 1.23 \, F_{r_L}^{0.2} & \text{if } F_{r_L} < 0.25, \end{cases} \]  
\[ N_{u,Coop} = 55 \, \dot{q}^{0.67} \, P_r^{0.12} \, MW^{-0.5} \, (-\log(P_r))^{-0.55} \, \frac{D_{in}}{\lambda_L}, \]  

where \( N_u \) denotes the Nusselt number, \( Fr \) the Froude number and \( \dot{q} \) the local heat flux. Subscripts ‘Watt’ and ‘Coop’ refer to correlations developed by Wattelet and Cooper, respectively [68].

The method developed by Steiner and Taborek (subscript ‘Ste’), as presented in Ref. [65], accounts for nucleate boiling and forced convection (subscript ‘FC’):

\[ \alpha_{Ste} = \left( \alpha_{Ste,NB}^3 + \alpha_{Ste,FC}^3 \right)^{0.33}, \]  
\[ \alpha_{Ste,NB} = \begin{cases} 0 & \text{if } \dot{q} \leq \dot{q}_{ons} \\ \alpha_0 C_F \left( \frac{\dot{q}}{\dot{q}_0} \right)^n Ste \, C_p \, C_D & \text{if } \dot{q} > \dot{q}_{ons}, \end{cases} \]  
\[ \alpha_{Ste,FC} = \alpha_{L0} \cdot \left\{ \left( 1 - x \right)^{0.01} \left[ \left( 1 - x \right) + 1.2 \, x^{0.4} \left( \frac{\rho_L}{\rho_V} \right)^{0.37} \right]^{-2.2} \right\}^{-0.5}, \]  
\[ \alpha_{L0} = 0.023 \, \frac{\lambda_L}{D_{in}} \, (R_e)_{L0}^{0.8} \, P_r_L^{0.4}, \]  
\[ \alpha_{V0} = 0.023 \, \frac{\lambda_L}{D_{in}} \, (R_e V_0)^{0.8} \, P_r_V^{0.4}, \]  
\[ \dot{q}_{ons} = \frac{2 \sigma \, T_{sat} \, \alpha_{L0}}{0.3 \times 10^{-6} \, \rho_V \, h_{LV}}, \]  
\[ \alpha_{L0} = 0.023 \, \frac{\lambda_L}{D_{in}} \, (R_e)_{L0}^{0.8} \, P_r_L^{0.4}, \]  
\[ \alpha_0 = 3580 \left( \frac{(dP/dT)_{sat,0}}{\sigma_0} \right)^{0.6}, \]  
\[ C_F = 0.435 \left( MW/2.016 \right)^{0.27}, \]  
\[ C_D = \left( \frac{D_0}{D_{in}} \right)^{0.4}, \]  
\[ C_P = 2.816 \, P_r^{0.45} + (3.4 + \frac{1.7}{1-P_r^2}) \, P_r^{3.7}, \]  
\[ n_{Ste} = 0.8 - 0.1 \times 10^{0.76 \, P_r}, \]  

where symbols with the subscript ‘o’, i.e. \( \alpha_0 \), \( \sigma_0 \) and \( (dP/dT)_{sat,0} \), denote reference values for these parameters at \( P_r = 0.1 \) and \( D_0 = 1 \text{ cm} \) [65], \((dP/dT)_{sat}\) denotes the slope of the saturated vapour curve, and the local heat flux at the onset of boiling is referred to as \( \dot{q}_{ons} \).
The asymptotic two-phase heat transfer correlation as developed by Liu and Winterton [69] (denoted here by subscript ‘LW’) is as follows:

\[
\alpha_{LW} = \left[ (F_{LW} \alpha_{L0})^2 + (S_{LW} \alpha_{Coop})^2 \right]^{0.5}, \tag{A.31}
\]

\[
F_{LW} = \left[ 1 + xP_f \left( \frac{\rho_l}{\rho_v} - 1 \right) \right]^{0.35}, \tag{A.32}
\]

\[
S_{LW} = \left[ 1 + 0.055F_{LW}^{0.1} Re_{L0}^{0.16} \right]^{-1}, \tag{A.33}
\]

where \( S_{LW} \) and \( F_{LW} \) are multiplication factors for the forced convection and nucleate boiling contributions to the overall heat transfer.

### A.2: Condenser heat transfer

In the condensing section, the two-phase heat transfer coefficient was estimated from correlations by Shah [70,71], Chaddock and Chato [63] and Boyko and Kruzhilin [72]. The Shah [70] correlation was used to estimate the average heat transfer coefficient when complete condensation of a saturated vapour occurs:

\[
\alpha_{Shah,1} = \left( 0.023 \frac{\lambda_l}{D_{in}} Re_{L0}^{0.8} Pr_{L0}^{0.3} \right) \left( 1.55 + \frac{0.09}{Pr_{L0}^{0.38}} \right). \tag{A.34}
\]

In Ref. [71], an improved correlation is presented where three distinct flow regimes are identified:

\[
\alpha_{Shah,2} = \begin{cases} 
\alpha_I & \text{if } J_g \geq (2.4Y + 0.73)^{-1}, \\
\alpha_{II} & \text{if } J_g \leq 0.89 - 0.93 \exp(-0.087Y^{-1.17}), \\
\alpha_I + \alpha_{II} & \text{else},
\end{cases} \tag{A.35}
\]

\[
Y = \left( \frac{1}{\alpha} - 1 \right) \frac{0.8}{Pr_{L0}^{0.4}}, \tag{A.36}
\]

\[
J_g = \frac{xG}{(g \rho_{in} \rho_v (\rho_l - \rho_v))^{0.5}}, \tag{A.37}
\]

\[
\alpha_I = \left( 0.023 \frac{\lambda_l}{D_{in}} Re_{L0}^{0.8} Pr_{L0}^{0.3} \right) \left( \frac{\mu_l}{14\mu_v} \right)^{n_{Shah}} \left( (1 - x)^{0.8} + \frac{0.38 (1-x)^{0.4}}{Pr_{L0}^{0.38}} \right), \tag{A.38}
\]

\[
\alpha_{II} = 1.23 Re_{L0}^{-0.33} \left( \frac{g \rho_l (\rho_l - \rho_v) \lambda_l}{\mu_l^2} \right)^{0.33}, \tag{A.39}
\]

\[
n_{Shah} = 0.0558 + 0.577 Pr_{L0}, \tag{A.40}
\]

where \( J_g \) is the dimensionless vapour velocity, \( \alpha_I \) and \( \alpha_{II} \) are heat transfer coefficients for two flow regimes, and \( n_{Shah} \) and \( Y \) are two dimensionless variables. This set of correlations is valid for vertical tubes.

Another correlation by Boyko and Kruzhilin (subscript ‘BK’) accounts for shear-driven condensation [72]:

\[
\alpha_{BK} = \left( 0.021 \frac{\lambda_l}{D_{in}} Re_{L0}^{0.8} Pr_{L0}^{0.43} \right) \left[ 1 + x \left( \frac{\rho_l}{\rho_v} - 1 \right) \right]^{0.5}. \tag{A.41}
\]
Finally, the estimation method accounting for shear and gravity driven condensation is not illustrated here, but a detailed description and working example can be found in Ref. [63].

**Appendix B: Cost correlations**

The values of $C_{BM,i}^0$ and $F_{p,i}$ for the single-phase sections of the heat exchangers and the turbine are determined using correlations from Ref. [76]. Data for factors $F_{M,i}$ and $F_{T,i}$ relating to these component units are taken from the same work. The correlations have the general form:

\[
\log_{10}[C_{BM,i}^0] = F_{1,i} + F_{2,i}\log[Z_i] + F_{3,i}*(\log[Z_i])^2, \tag{B.1}
\]

\[
\log_{10}[F_{p,i}] = K_{1,i} + K_{2,i}\log[P_i] + K_{3,i}*(\log[P_i])^2, \tag{B.2}
\]

\[
C_{BM,i} = \frac{\text{CEPCI}_{2017}}{\text{CEPCI}_{\text{reference}}}(B_{1,i} + B_{2,i}F_{p,i}F_{T,i}F_{M,i})C_{BM,i}^0, \tag{B.3}
\]

where $F_{1,i}$, $F_{2,i}$, $F_{3,i}$, $K_{1,i}$, $K_{2,i}$, $K_{3,i}$, $B_{1,i}$, and $B_{2,i}$ are equipment specific coefficients documented in Turton [76], $Z_i$ is the equipment specific size parameter, which differs between equipment types, $P_i$ is the gauge pressure (in barg), and if $P_i \leq 40$ barg then $F_{p,i} = 1$ for the single-phase sections of the heat exchangers.

Similarly, the values of $C_{BM,i}^0$ and $F_{p,i}$ for the two-phase sections of the heat exchangers and the pump are obtained through correlations by Seider et al. [77]. Data for factors $F_{M,i}$ and $F_{T,i}$ of these component units are taken from the same work. The correlations have the general form:

\[
\ln[C_{BM,i}^0] = F_{1,i} + F_{2,i}\ln[Z_i] + F_{3,i}(\ln[Z_i])^2 + F_{4,i}(\ln[Z_i])^3 + F_{5,i}(\ln[Z_i])^4, \tag{B.4}
\]

\[
F_{p,i} = K_{1,i} + K_{2,i}\left(\frac{P_i}{600}\right) + K_{3,i}\left(\frac{P_i}{600}\right)^2, \tag{B.5}
\]

where Eq. B.5 is only valid for the heat exchangers, $P_i$ is the gauge pressure (in barg), and if $P_i \leq 600$ psig then $F_{p,i} = 1$ for the two-phase section of the heat exchangers. No $F_{p,i}$ value is given for pumps. All parameters used in these correlations for each component unit are stated in Tables B.1 and B.2.

**Table B.1:** Coefficients and sizing parameters ($Z_i$) used in Eqs. B.1 to B.5. Here, $S$ denotes volumetric flow rate in gallons per minute times the square root of the pump pressure head in feet.

<table>
<thead>
<tr>
<th>Component</th>
<th>$F_{1,i}$</th>
<th>$F_{2,i}$</th>
<th>$F_{3,i}$</th>
<th>$F_{4,i}$</th>
<th>$F_{5,i}$</th>
<th>$Z_i$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-phase HEX</td>
<td>3.3444</td>
<td>0.2749</td>
<td>-0.0472</td>
<td>-</td>
<td>-</td>
<td>$A_i$ [m²]</td>
<td>[76]</td>
</tr>
<tr>
<td>Two-phase HEX</td>
<td>9.5638</td>
<td>0.532</td>
<td>-0.002</td>
<td>-</td>
<td>-</td>
<td>$A_i$ [ft²]</td>
<td>[77]</td>
</tr>
<tr>
<td>Radial turbine</td>
<td>2.2476</td>
<td>1.4965</td>
<td>-0.1618</td>
<td>-</td>
<td>-</td>
<td>$\dot{W}_{\text{turb}}$ [kW]</td>
<td>[76]</td>
</tr>
<tr>
<td>Pump motor</td>
<td>5.8259</td>
<td>0.1314</td>
<td>0.053255</td>
<td>0.028628</td>
<td>0.003555</td>
<td>$\dot{W}_{\text{pump}}$ [HP]</td>
<td>[77]</td>
</tr>
<tr>
<td>Pump casing</td>
<td>9.7171</td>
<td>-0.6019</td>
<td>0.0519</td>
<td>-</td>
<td>-</td>
<td>$S$ [gpm $\sqrt{\text{ft}}$]</td>
<td>[77]</td>
</tr>
</tbody>
</table>
Table B.2: Coefficients used in Eqs. B.1 to B.5.

<table>
<thead>
<tr>
<th>Component</th>
<th>$K_{1,i}$</th>
<th>$K_{2,i}$</th>
<th>$K_{3,i}$</th>
<th>$B_{1,i}$</th>
<th>$B_{2,i}$</th>
<th>$F_{M,i}$</th>
<th>$F_{T,i}$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-phase HEX</td>
<td>0.6024</td>
<td>-0.912</td>
<td>0.3327</td>
<td>1.74</td>
<td>1.55</td>
<td>1</td>
<td>1</td>
<td>[76]</td>
</tr>
<tr>
<td>Two-phase HEX</td>
<td>0.851</td>
<td>0.1292</td>
<td>0.0198</td>
<td>1.74</td>
<td>1.55</td>
<td>1</td>
<td>1</td>
<td>[77]</td>
</tr>
<tr>
<td>Radial turbine</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[76]</td>
</tr>
<tr>
<td>Pump motor</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>1.4</td>
</tr>
<tr>
<td>Pump casing</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>1</td>
<td>2.7</td>
</tr>
</tbody>
</table>

The CEPCI values used in this paper to account for inflation costs are listed in Table B.3.

Table B.3: CEPCI values corresponding to different years.

<table>
<thead>
<tr>
<th>Year</th>
<th>CEPCI</th>
</tr>
</thead>
<tbody>
<tr>
<td>2001</td>
<td>397.0</td>
</tr>
<tr>
<td>2006</td>
<td>500.0</td>
</tr>
<tr>
<td>2013</td>
<td>567.3</td>
</tr>
<tr>
<td>2014</td>
<td>576.1</td>
</tr>
<tr>
<td>2017</td>
<td>556.8</td>
</tr>
</tbody>
</table>

For the component units for which $C_{0,BM,i}$ is determined from Turton [63], CEPCI\textsubscript{2001} values are used and for those determined from Seider et al. [64], CEPCI\textsubscript{2006} value are used in Equation B3. The costs for the generator are estimated using the correlation from Toffolo et al. [88]:

$$C_{BM,i} = 1.5 \times 1,850,000 \left(\frac{\dot{W}_{\text{turb}}}{11,800}\right)^{0.94},$$  \hspace{1cm} (B.6)

where $\dot{W}_{\text{turb}}$ is in kW. CEPCI\textsubscript{2013} values are used to convert the costs to 2017, and the costs of the generator gearbox are estimated as amounting to 40% of the generator costs [89].

Appendix C: $T$-$s$ diagrams of MINLP solutions

In this Appendix, the $T$-$s$ diagrams, critical pressure, critical temperature and normal boiling point ($T_{bn}$) of the working fluids presented in Tables 5 and 6 are shown in Fig. C.1. Only novel fluids, of which the properties are not available in REFPROP, are presented here.
Figure C.1: $T$-$s$ diagrams of novel working fluids presented in Tables 5 and 6. Only $T$-$s$ diagrams of working fluids which are not present in the REFPROP database are shown.

Table C.1: Selection of physical properties of novel working fluids presented in Tables 5 and 6.

<table>
<thead>
<tr>
<th>S/N</th>
<th>Systematic name</th>
<th>$T_{cr}$ [°C]</th>
<th>$P_{cr}$ [bar]</th>
<th>$T_{bn}$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,3-butadiene</td>
<td>152</td>
<td>43</td>
<td>-6</td>
</tr>
<tr>
<td>2</td>
<td>4,4-dimethyl-2-pentene</td>
<td>234</td>
<td>30</td>
<td>63</td>
</tr>
<tr>
<td>3</td>
<td>3,3-dimethyl-1,4-pentadiene</td>
<td>240</td>
<td>31</td>
<td>64</td>
</tr>
<tr>
<td>4</td>
<td>4-methyl-2-pentene</td>
<td>219</td>
<td>33</td>
<td>51</td>
</tr>
<tr>
<td>5</td>
<td>2,2-dimethylbutane</td>
<td>216</td>
<td>32</td>
<td>48</td>
</tr>
<tr>
<td>6</td>
<td>3-methyl-1,4-pentadiene</td>
<td>224</td>
<td>35</td>
<td>52</td>
</tr>
<tr>
<td>7</td>
<td>2-pentene</td>
<td>204</td>
<td>37</td>
<td>37</td>
</tr>
<tr>
<td>8</td>
<td>1,4-pentadiene</td>
<td>196</td>
<td>38</td>
<td>29</td>
</tr>
</tbody>
</table>

References


[27] J. A. Schwöbel, M. Preißlinger, D. Brüggemann and A. Klamt, "High-throughput screening of working fluids for the organic Rankine cycle (ORC) based on conductor-like screening model for realistic solvation (COSMO-RS) and
integrating molecular design into thermo...


[70] M. M. Shah, "A general correlation for heat transfer during film condensation inside pipes,"


