On the use of SAFT-VR Mie for assessing large-glide fluorocarbon working-fluid mixtures in organic Rankine cycles

Oyeniyi A. Oyewunmi, Aly I. Taleb, Andrew J. Haslam, Christos N. Markides

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

HIGHLIGHTS
- SAFT-VR Mie produces highly accurate thermodynamic properties of ORC fluid systems.
- Limiting superheating to a minimum leads to cycles with superior performance.
- Generally, cycles with pure working fluids are more powerful and cost effective.
- Large-glide fluid mixtures are attractive in applications with limited cooling resources.

ABSTRACT
By employing the SAFT-VR Mie equation of state, molecular-based models are developed from which the thermodynamic properties of pure (i.e., single-component) organic fluids and their mixtures are calculated. This approach can enable the selection of optimal working fluids in organic Rankine cycle (ORC) applications, even in cases for which experimental data relating to mixture properties are not available. After developing models for perfluoroalkane (n-C4F10 + n-C10F22) mixtures, and validating these against available experimental data, SAFT-VR Mie is shown to predict accurately both the single-phase and saturation properties of these fluids. In particular, second-derivative properties (e.g., specific heat capacities), which are less reliably calculated by cubic equations of state (EoS), are accurately described using SAFT-VR Mie, thereby enabling an accurate prediction of important working-fluid properties such as the specific entropy. The property data are then used in thermodynamic cycle analyses for the evaluation of ORC performance and cost. The approach is applied to a specific case study in which a sub-critical, non-regenerative ORC system recovers and converts waste heat from a refinery flue-gas stream with fixed, predefined conditions. Results are compared with those obtained when employing analogue alkane mixtures (n-C4H10 + n-C10H22) for which sufficient thermodynamic property data exist. When unlimited quantities of cooling water are utilized, pure perfluorobutane (and pure butane) cycles exhibit higher power outputs and higher thermal efficiencies compared to mixtures with perfluorodecane (or decane), respectively. The effect of the composition of a working-fluid mixture in the aforementioned performance indicators is non-trivial. Only at low evaporator pressures (<10 bar) do the investigated mixtures perform better than the pure fluids. A basic cost analysis reveals that systems with pure perfluorobutane (and butane) fluids are associated with relatively high total costs, but are nevertheless more cost effective per unit power output than the fluid mixtures (due to the higher generated power). When the quantity of cooling water is constrained by the application, overall performance deteriorates, and mixtures emerge as the optimal working fluids.

1. Introduction
The recovery and utilization of low- and medium-grade (i.e., temperature) waste heat has been identified as a major path-
(e.g., mechanical, hydraulic, or electrical), thus allowing improvements to overall efficiency, minimization of primary-fuel consumption, and consequently, emission abatement.

Beyond the conversion of low- and medium-grade waste-heat, increased attention is being directed at technologies capable of utilizing heat in this temperature range that promise to alleviate the challenges relating to energy and the environment either: (1) by maximizing the overall efficiency of fossil-fuel use, examples of which are energy integration through the matching of thermal sources and sinks primarily in industrial and commercial sites, and also co-generation or combined heat and power (CHP) and tri-generation systems in a range of applications across scales; or (2) by circumventing the need for fossil-fuels altogether, such as by harnessing heat from renewable energy sources (e.g., solar, geothermal). In particular, a growing interest has been observed in organic Rankine cycle (ORC) systems due to their applicability to the efficient conversion of lower-grade heat to useful power. ORC systems generate power by using organic working fluids in a similar manner to conventional steam-cycle power plants. By employing suitably designed ORC systems, power can be generated by utilizing a broad range of thermal energy sources, including harvested waste heat in industrial and commercial settings, recovered heat in biomass/biogas cogeneration applications, as well as hot fluid-streams in lower-temperature geothermal resources or from non-/low-concentrated solar collectors, amongst many others.

ORCs have lower thermal efficiencies (defined as the ratio of net work output to the heat input from the heat source; see Eq. (13)) than those associated with large-scale, centralized fossil-fuelled power plants, due to the lower temperature of the heat sources involved. Nevertheless, the associated energy sources (mentioned above) are typically more easily accessible, abundant and affordable than the fuels used in conventional power plants. The fuel costs in such plants can account for up to two-thirds of the leveraged costs (i.e., total costs, including capital expenditure, operation, maintenance, and all overheads) of electricity generation over the lifetime of a plant’s operation. Therefore, the aim in lower-grade heat conversion technologies, such as ORCs, at least from an economic viability perspective, is one of maximizing their power output while minimizing the dominant investment and capital costs [4,5]. Efficiency is important only in as much as it contributes to this aim. With this in mind, in the present paper we consider both the performance and cost of relevant ORC systems.

A number of particularly interesting studies that have focused on ORC system performance, specifically from a second-law perspective, have revealed that the evaporator and condenser together account typically for over 70% of the total lost work (exergy destruction) in the overall cycle [6–9], with the exergy loss in the evaporator amounting to approximately 1.5–2 times that lost in the condenser. The thermodynamic loss in these components arises from the irreversibility associated with the heat transfer between the external heat source (or sink) stream and the working fluid across a finite temperature difference. In most cases, this loss is additionally aggravated when employing single-component working fluids due to the isothermal nature of the isobaric phase-change process through the evaporator (and condenser). (In practice, small pressure drops are observed in these heat-exchange components, but these are not associated with any significant temperature changes.) This gives rise to the well-known pinch-point, away from which the temperature differences between the heat source/sink stream and the working fluid are considerably higher, thereby increasing the exergy losses.

The aforementioned shortcoming of using pure working fluids in ORCs has been motivating research into the deployment of zeotropic mixtures as working fluids. These fluid mixtures do not suffer from such a temperature limitation since they are known to undergo non-isothermal phase change (a so-called ‘temperature glide’) at constant pressure. This gives rise to an increasing boiling point during heat addition in the evaporator (e.g., see Fig. 9), resulting in an improved thermal match between the heat-source and working-fluid mixture streams (i.e., a smaller average temperature difference between the two streams) in this heat exchanger and, consequently, a reduced associated thermodynamic (exergy) loss in the process, and an improved thermal efficiency and net power output from the cycle. Such an improved overall thermodynamic performance, arising from improvements to the heat-addition process, can offer benefits in terms of smaller (and more affordable) ORC systems [10,11] while shifting the dominant component of the cycle’s exergy losses to the expander [12] as opposed to the case of a pure (single-component) fluid where the heat-exchange processes dominate the exergy losses, as mentioned earlier.

A number of previous studies have demonstrated the potential benefits of exploiting the temperature glide of working-fluid mixtures in designing more-efficient and power-dense cycles. Specifically, suitable binary working-fluids have been shown to increase the power output of ORC systems in specific applications by up to 20% and thermal efficiencies by over 15% relative to single-component fluids [13]. An experimental study of a solar-ORC engine with R245fa + R152a working fluid [11] led to the conclusion that the mixture offers improved collector/cycle thermal efficiencies and expander-size reductions when compared to an equivalent cycle operating with pure R245fa. Other working-fluid mixtures investigated include isobutene + isopentane and R227ea + R245fa with geothermal-ORCs [14,15], the quaternary mixture of R125 + R123 + R124 + R134a in the case of a heat recovery application [16], and a number of others in the study by Lecompte et al. [8], and others. These efforts suggest that working-fluid mixtures can be more effective with low-temperature heat sources than with higher-temperature sources. Furthermore, from an environmental perspective, the physical and chemical properties of promising working fluids can also be altered by selecting and varying the composition of appropriate fluid mixtures [12]. Thus the global-warming and ozone-depletion potentials of prospective ORC working fluids can be significantly reduced.

Although these studies have highlighted some of the potential benefits of employing working-fluid mixtures in ORC systems, research into the exact benefits of the employment of working-fluid mixtures and the identification of application-specific optimal fluids is still in its early stages. One obstacle to this endeavour arises from the fact that the suitability of a working fluid is a strong function of the particular cycle, designed typically for a custom application. Therefore, the identification of an optimal working fluid from a large range of potential candidates is not possible without detailed information on the specific application. In many applications, the main goal is power generation and there are sufficiently large quantities of cooling water available and affordable. In this case, small glides during condensation will always be preferred for best performance. Most studies into ORCs with working-fluid mixtures have focused on this type of application [10–16]. If this is not the case, however, the thermodynamically optimal working fluids will be ones that best match the varying temperature profiles of the heat source and sink streams (through both the evaporator and condenser), which, depending on the specific application, may be associated with either small or large glides [2]. Such heat sources and sinks appear as external boundary conditions to the ORC systems being designed, and the designer typically has no control over their characteristics. In these cases, efforts to consider fluid mixtures with large temperature glides are important, for example, where ORC systems are being considered in applications with limited quantities of cooling water [17,18], which is actually a desirable feature in itself, in CHP
applications [19,20] and in energy integration [21–25] where the heat sink stream has been pre-identified and is associated with a significant temperature variation, thus requiring a temperature glide with a similar magnitude on the condensing side of the power cycle.

A second challenge concerns the availability of and access to accurate thermodynamic (and transport) property data and phase-behavior information, especially in the case of mixtures of dissimilar fluids that would exhibit large temperature glides. Databases such as the NIST WebBook [26] and fluid-data software packages (e.g., REFPROP [27] and CoolProp [28]) have been commonly used in designing single-component working fluids for ORC systems. REFPROP and CoolProp employ equations of state that contain large numbers of parameters, enabling excellent correlations of experimental data, and thereby these software packages provide outstanding descriptions of the thermodynamics of fluids that have undergone extensive experimental study and for which data are plentiful. On the other hand, the success of multi-parameter, correlative equations is less clear when applied to fluids for which data are scarce, especially in terms of thermodynamic states outside the regions of the experiments from which the correlations were made; moreover, this situation may be exacerbated when using mixing rules (which introduce an added level of uncertainty) to obtain mixture properties. A particular difficulty lies in the reliable evaluation of heat transfer coefficients and specific heat capacities for such working-fluid mixtures, especially as these quantities can depend on mixture compositions in a non-trivial fashion.

Our current understanding of the challenges and potential benefits of using advanced working fluids in ORCs can be vastly improved by the development of powerful whole-system optimization platforms, featuring accurate and reliable property-prediction models for both pure fluids and fluid mixtures. To this end, computer-aided molecular design (CAMD) offers a viable and promising approach for the simultaneous optimization of both the working fluid (including mixtures) and the design of the ORC system [29,30], extending to the design of novel fluid substances and mixtures, the specification of optimal cycle conditions, as well as the implementation of innovative, advanced system architectures. For this purpose, reliable and simple descriptions of the working fluids at the molecular level, and of the molecular interactions of different components for the case of mixtures, are much desired. Recently, research groups have begun to explore the use of advanced molecular models (e.g., PC-SAFT [31,32]) for fluids with this in mind (e.g., [33–36]), but more work is needed before we are in a position to understand fully the role of working-fluid selection (and ultimately true molecular design, leading to novel fluids) in determining key thermodynamic properties and system variables, and thereby in maximizing the overall techno-economic indicators of ORC systems [5].

With the primary objective of developing reliable molecular models for ORC working fluids (both pure and mixtures), in the current study we employ the SAFT-VR Mie equation of state [37] – a recent version of the statistical associating fluid theory (SAFT) for molecules interacting through potentials of variable range [38] – to investigate the selection of working-fluid mixtures and component mixing ratios for an ORC application from both a thermodynamic and an economic perspective. First, we present a simple mathematical model of an ORC system in a pre-selected application, including a model for the evaluation of the relative costs of the system’s components that enables a techno–economic comparison of performance with respect to working-fluid composition. Mixtures of two relatively dissimilar fluids are specifically investigated in order to test the potential of the present approach in predicting thermodynamic properties in this particularly challenging scenario. The molecular models of the working fluids of choice (alkanes and perfluoroalkanes) are then developed using SAFT-VR Mie, after which the thermodynamic-property calculations carried out for the fluid mixtures are validated against available experimental data. These fluids are known to be environmentally benign with zero ozone-depletion potentials (ODPs) and low global-warming potentials (GWPs) compared to high-performance alternatives, e.g., CFC-12 [39,40]. The perfluoroalkanes, in particular, are stable, have high autoignition temperatures [41,42], and have been recommended as replacements of fluids with high ODP and GWP [40]. These aspects are of significant importance in the ultimate selection (or design) of working fluids for ORC applications. By incorporating the fluid property data calculated by SAFT-VR Mie within ORC thermodynamic and cost models, we then investigate the effect of selecting various working-fluid mixtures on ORC efficiency and power production, taking into account implications concerning the sizes and costs of the various ORC system components. The paper concludes by summarizing the key knowledge and future prospects garnered from the fluid models and simulations.

The present paper goes beyond a previous study [5], which dealt with butane–decane mixtures in smaller ORC systems (<4 MW) for waste-heat conversion, by: (i) considering new fluid mixtures (specifically, perfluorocarbons) for which experimental data do not yet exist as a direct demonstration of the strength of the proposed SAFT–VR approach; and (ii) examining larger ORC systems in an application with power outputs up to 30 MW, and performance under a revised condenser condition according to which the pressure cannot drop below 1 bar, the temperature cannot drop below 30 °C and where a finite cooling flow is available, all of which reflect practical aspects in the implementation of these systems. Interestingly, it will be shown here that under these conditions the conclusions concerning ORC system cost and performance are in direct opposition to the conclusions in Ref. [5], even when the same alkane working-fluid system is considered.) The application of SAFT–VR Mie to the new chemical class (perfluorocarbons) and the validation of all fluid–property predictions are also expanded by comparing our predictions to experimentally obtained values in the $T$–$\rho$ and $T$–$c_p$ spaces.

### 2. Organic Rankine cycle modeling

It its simplest form, the organic Rankine cycle (ORC) consists of four basic processes undertaken by an organic working fluid, each requiring separate dedicated components. Two of these are heat exchangers, one for high-pressure heat addition to the working fluid from the heat source (evaporator), and another for lower-pressure heat rejection from the cycle to the heat sink (condenser). An expander/turbine generates power by expanding the working fluid from the high (evaporator) pressure to the low (condenser) pressure. Finally, a pump is required for working-fluid circulation and re-pressurization from the low-pressure in the condenser to the higher pressure in the evaporator. A typical ORC setup along with the associated $T$–$s$ diagram is shown in Fig. 1. The states of the working fluid at labeled points through the cycle are indicated on the $T$–$s$ diagram. Depending on the application, additional components may be required in practice, including waste-heat/process stream and/or coolant-fluid pumps, along with equipment items such as motors, alternators, separators, tanks, seals, piping and instrumentation (gauges, valves, etc.).

An additional heat exchanger may be used as a regenerator (also referred to as a recuperator) to preheat the working fluid after pressurization. This utilizes some of the available thermal energy in the working fluid at the outlet of the expander thus lowering the total external heat requirement from the heat source and improving efficiency. Nevertheless, the inclusion of a regenerator
invariably increases the complexity and cost of an ORC system. The authors take the view that minimizing capital and investment costs is of paramount importance, especially in distributed, small- to medium-scale waste-heat conversion and energy integration applications, and therefore a regenerator was not considered in the present study; rather, the problem definition is to maximize the power output of a simple, non-regenerative ORC, while considering indicative system costs.

2.1. Thermodynamic model of the cycle

With the assumption that the ORC engine is operating at steady state conditions, dynamic relations are not necessary and steady-state energy balances suffice for a thermodynamic cycle analysis. The resulting model equations for the processes depicted in Fig. 1 are stated briefly below, for completeness.

2.1.1. Working-fluid pump (State 1 → State 2)

The pump delivers working fluid from a pre-specified condensing pressure to a pre-specified evaporating pressure. State 1 (in Fig. 1) is determined by the condensing pressure under the assumption that there is no sub-cooling of the working fluid (i.e., saturated liquid). The fluid properties (temperature, T; specific entropy, s; and specific enthalpy, h) for State 1 are thus functions of the condensing pressure and mixture composition x only:

\[ \{T_1, s_1, h_1\} = f(P_{\text{at}}) \]  

State 2 can be determined by considering the imposed evaporating pressure \( P_{\text{ev}} \) and a given isentropic efficiency value for the pump defined as:

\[ \eta_{\text{is,pump}} = \frac{h_2(P_{\text{ev}}) - h_1}{h_2 - h_1} \]  

where \( h_2 \) is the enthalpy of the working fluid following an isentropic process from State 1 to the evaporating pressure \( P_{\text{ev}} \). The fluid properties at State 2 are then calculated from:

\[ \{T_2, s_2\} = f(P_{\text{ev}} x, h_2) \]  

with \( h_2 \) having been previously evaluated from Eq. (2).

Thus, the power required to pump the working fluid from \( P_{\text{at}} \) to \( P_{\text{ev}} \) (i.e., State 1 to State 2) is given by the working-fluid enthalpy change through the pump:

\[ W_{\text{pump}} = m_{\text{at}}(h_2 - h_1), \]  

where \( m_{\text{at}} \) is the mass flow-rate of the fluid through the pump.

2.1.2. Heat addition (State 2 → State 3)

The working fluid in the liquid state (State 2) is heated in the evaporator using heat extracted from the heat source and leaves the evaporator as a saturated vapour (at its dew point at the evaporating pressure) or a superheated vapour (State 3). This is taken to be an isobaric process, which is justified by assuming a relatively small pressure drop in the flow through the heat exchanger relative to the pressure in this component, i.e., \( P_{\text{at}} \). The temperature of the working fluid at State 3 is fixed as the dew-point temperature \( T_{\text{dew}} \) at the evaporating pressure, \( P_{\text{ev}} \), plus a variable superheat temperature difference (\( \Delta T_3 \)) from the dew point, set by the degree of superheating. The degree of superheating, \( d_{\text{SH}} \), varied between 0 (for non-superheated cycles) and 1 (for maximum-superheated cycles), is defined by:

\[ T_3 = d_{\text{SH}}(T_{3\text{max}} - T_{\text{dew}}) \]  

where \( T_{3\text{max}} \) is the maximum possible superheat temperature (usually the heat-source temperature minus a pre-specified minimum pinch temperature-difference), such that:

\[ T_3 = T_{\text{dew}} + \Delta T_3 \]  

Once State 3 has been defined, all other properties of the working fluid at the evaporator exit (and expander/turbine inlet) can be found from:

\[ \{s_3, h_3\} = f(P_{\text{at}}, T_3) \]  

Assuming no heat losses, the heating rate required to evaporate the working fluid and raise its temperature from \( T_2 \) to the bubble point, and to superheat it from the dew point to \( T_3 \), is equal to the rate of heat extraction from the heat source, \( Q_{\text{in}} \):

\[ \dot{Q}_{\text{in}} = m_{\text{at}}(h_3 - h_2) = m_{\text{at}}c_p h_3(T_{\text{in}} - T_{\text{out}}) \]  

where \( m_{\text{at}} \) is the mass flow-rate of the heat-source stream, \( c_p h_3 \) is its specific heat capacity, and \( T_{\text{in}} \) and \( T_{\text{out}} \) are the inlet and outlet temperatures of this stream at the evaporator.

2.1.3. Expansion machine (State 3 → State 4)

A real expansion process is not isentropic due to irreversible thermal and mechanical loss mechanisms. This is accounted for by defining an isentropic efficiency for the expander:

\[ \eta_{\text{is,exp}} = \frac{h_3 - h_4}{h_3 - h_{4\text{a}}(P_{\text{at}})} \]  

where \( h_{4\text{a}} \) would have been the enthalpy of the working fluid following an ideal, isentropic expansion process from State 3 down
to the condensing pressure $P_{41}$. Having calculated $h_3$ from Eq. (9), and given a knowledge of the condensing pressure, all other State 4 properties are then calculated at the end of the non-isentropic expansion process:

$$\{T_4, s_4\} = f(P_{41}, x, \eta_{hs, exp}).$$  

(10)

Furthermore, the power generated by the expansion of the working fluid from $P_{23}$ to $P_{41}$ is:

$$W_{exp} = m_{w} (h_4 - h_3).$$  

(11)

### 2.1.4. Heat rejection (State 4 → State 1)

The low-pressure ($P_{41}$) expanded fluid is condensed to a liquid state at constant pressure typically using water at ambient conditions as a heat-rejection medium. The expression for the rate of heat rejection in the condenser is similar to that of the heat input in the evaporator:

$$Q_{out} = m_{w} (h_4 - h_1) = m_{cs} c_{cs} (T_{cs, out} - T_{cs, in}).$$  

(12)

A noteworthy novelty of the present work is highlighted at this point. The conditions in the condenser are imposed to ensure that:

(i) the pressure in this component remains at or above atmospheric pressure (1 bar), thus preventing air ingress into the system; while,

(ii) the corresponding temperature remains above the cooling-stream temperature ($20^\circ C$; see Section 2.2) plus a specified minimum pinch temperature difference ($10^\circ C$; Section 2.1.6) to permit heat rejection. The selection of the heat-rejection conditions (in particular, of the condensation pressure and cooling-stream flow-rate) is described in Section 4.

### 2.1.5. Degrees of freedom and thermodynamic cycle solution

Eqs. (1)–(12) represent the thermodynamic model of the sub-critical, non-regenerative ORC system under consideration. The equations in Section 2.1.1 are solved by specifying the composition and mass flow-rate of the working fluid, the evaporating and condensing pressures, and the pump’s isentropic efficiency. The degree of superheating and the heat-source characteristics present a consistent set of variables for the equations in Section 2.1.2. In a similar manner, the expander’s isentropic efficiency and the coolant characteristics represent consistent variable sets for Sections 2.1.3 and 2.1.4, respectively. Finally, the thermal efficiency of the ORC is calculated as the ratio of the net power output from the system (expander/turbine minus pumping power) to the rate of heat input from the source:

$$\eta_{th, ORC} = (W_{exp} - W_{pump})/Q_{in}. \quad \text{(13)}$$

### 2.1.6. Heat exchangers

The model described above captures the thermodynamic characteristics of the ORC. Eqs. (8) and (12) maintain the overall heat-transfer balance between the hot-side and cold-side streams in the two heat exchangers. However, it is important to impose relationships between the hot-side and the cold-side fluid temperatures in the two heat-exchanger arrangements in order to ensure that the second law is not violated at any point along the length of the heat exchangers (i.e., that heat is always transferred from the higher- to the lower-temperature fluid, across a finite temperature difference), thereby maintaining the feasibility of the overall heat transfer design represented in the equations above. Specifying a minimum pinch-point temperature difference between the hot-side and cold-side fluid streams along the length of the heat exchangers maintains the feasibility of both heat exchangers and hence the validity of the solution of the model equations.

First, the evaporator is conceptualized as comprising three sections, one each for the preheating, evaporation and superheating processes of the working fluid. Eq. (8), which represents the rate of heat addition to the working fluid, can thereby be rewritten as:

$$\dot{Q}_{in} = m_{w} c_{p, w} (T_{bub, p_{23}} - T_2) + m_{w} c_{p, w} (T_{dew, p_{23}} - T_3 - T_{dew, p_{23}}).$$  

(14)

Here, $c_{p, w}$ and $c_{p, v}$ are the specific heat capacities of the working fluid in the sub-cooled and superheated states respectively, while $p_{23}$ represents the latent heat of vaporization (all at $P_{23}$).

The enthalpy and temperature profiles in the heat-source and the working-fluid streams through each section of the evaporator is discretized into segments. By calculating the temperature difference between the heat source and the working fluid across each segment, one can examine the profile of the temperature difference through the exchanger. Discretizing each section into 20 segments is found to be sufficient to obtain smooth and continuous profiles for the heat-source and working-fluid streams. Thus, the thermal energy balance in any segment ‘i’ of the heat exchanger can be written as:

$$m_{w} c_{p, w} (T_i - T_{i-1}) = m_{hs} c_{p, hs} (T_{hs, i-1} - T_{hs, i}).$$  

(15)

The pinch point in the heat exchanger is the segment with the lowest temperature difference ($\Delta T_{mp} = \min (T_{hs, i} - T_i, \forall i)$ between the heat source and the working fluid. The feasibility of the heat exchanger is thus ensured by specifying that the pinch-point temperature difference is not lower than the stated minimum of 10°C.

The condenser is treated as comprising two sections: the desuperheating section, and the condensing section. Both of these are discretized into segments in a similar manner to the sections in the evaporator, and the pinch-point temperature difference is specified to be not less than the minimum of 10°C. One thus obtains:

$$Q_{out} = m_{w} c_{p, w} (T_4 - T_{dew, p_{41}}) + m_{w} c_{v} (T_4).$$  

(16)

Constant specific heat capacities are assumed for both the heat source and the cooling fluids.

### 2.2. Case study: Waste-heat source and heat-rejection medium

In the present study we consider a waste-heat conversion application with ORC systems, where the heat source is taken to be a flue-gas stream from a gas-fired boiler in a refinery, composed of nitrogen, oxygen, steam and carbon dioxide. The conditions of the flue-gas waste-heat stream are known from direct measurements at the boiler exhaust (flow rate of 560 kg/s, temperature of 330 °C), and the specific heat capacity of the flue gas can be evaluated from the known constituent compounds (giving a value of 1.07 kJ/kg K). The cooling stream is a flow of water at 20 °C and at atmospheric pressure (full details are given in Section 4).

### 2.3. Costs for economic evaluation

The first estimate of the capital cost of the investigated ORC system is made by adding the costs of each of its four major constituent components with the ultimate goal of investigating the role of working-fluid mixtures in affecting the capital costs of these engines. Thus, the costs of the aforementioned components (heat exchangers, pump and expander)—which represent the largest contribution (typically 50–70%) to the total installed costs of an engine in a waste-heat application [43, 44]—are evaluated and summed. The optimal compromise between performance, size and cost will in practice come from the system purchaser, installer or user. Therefore, the outputs of the economic evaluation are reported both in terms of absolute costs (in £) and in terms of the cost per unit of power produced from the engine (in £/kW), in order to provide the broadest possible examination of these results.
In more detail, the heat exchanger costs are derived by using the C-value method [45], combined with the ESDU 92013 chart that contains cost correlations for different heat-exchanger types. For simplicity in this work, the evaporator and condenser are specified as being of the shell-and-tube type. The rate of heat transferred across a heat exchanger of contact area \( A \) can be described by an overall heat-transfer coefficient \( U \), according to:

\[
\dot{Q} = UA\Delta T_{lm}, \tag{17}
\]

where the logarithmic-mean temperature difference, \( \Delta T_{lm} \), is defined as (for the evaporator):

\[
\Delta T_{lm} = \frac{(T_{hi,in} - T_3) - (T_{hi,out} - T_2)}{\ln((T_{hi,in} - T_3)/(T_{hi,out} - T_2))}. \tag{18}
\]

The \( \Delta T_{lm} \) in the condenser is calculated in a similar manner.

The cost of a heat exchanger is a strong function of its size, which is related to the area available for heat transfer \( A \). Various empirical methods and relationships (typically power laws) have been developed to estimate heat-exchanger costs in terms of a cost per unit area \( C \). A challenge of such methods lies in the complex definition of the heat-transfer area for different types of heat exchangers. In the \( C \)-value method employed in the present study the heat-exchanger costs are estimated using the knowledge of the heat load, \( Q \), and the average available temperature difference \( \Delta T_{lm} \). A cost factor \( C \) is defined as the cost per unit \( (UA) \) or per unit \( Q/\Delta T_{lm} \), which avoids the challenges of separately quantifying the area and overall heat-transfer coefficients involved.

The ESDU 92013 chart contains tabulated values of overall heat-transfer coefficients, \( U \), and cost factors, \( C \), for different cold-side and hot-side fluids at fixed values of \( Q/\Delta T_{lm} \). The values of \( Q/\Delta T_{lm} \) are calculated from Eqs. (8), (12), (14), (16) and (18), and the \( 'U' \ (W/m^2K') \ and 'C' (€/(W/K))' values are obtained using the logarithmic interpolation:

\[
C = \exp \left\{ \ln C_1 + \ln(C_1/C_2) \left[ \ln \left( \frac{Q/\Delta T_{lm}}{Q/\Delta T_{lm}} \right) \right] - \ln \left( \frac{Q/\Delta T_{lm}}{Q/\Delta T_{lm}} \right) \right\}, \tag{19}
\]

The \( C \) value is then multiplied by \( Q/\Delta T_{lm} \) (and adjusted for inflation) to obtain the cost of the heat exchangers. On the ESDU 92013 chart, the \( C \)-values under ‘Low Viscosity Organic Liquids’ and ‘Low Pressure Gas’ are used for the cold fluid side (working fluid) and hot fluid side (flue gas) respectively for the evaporator. For the condenser, the \( C \)-values under ‘Low Viscosity Organic Liquids’ and ‘Process Water’ are used for the hot-fluid side (working fluid) and cold-fluid side (cooling water), respectively.

Cost data for suitable ORC turbo-expanders and positive-displacement expanders were collected by means of a market survey, similarly to Ref. [44]. Currently, positive-displacement expanders have limited commercial availability as off-the-shelf items specifically for use in power generation. Costs were therefore based on equivalently sized positive-displacement compressors. The expander cost was described as a function of its inlet volumetric flow-rate \( (V_i) \) and the pressure ratio \( (P_{hi}/P_{at}) \). The data surveyed covered a wide range of operating conditions with flow rates ranging from \( \sim 100 \) cm\(^3\)/s to 0.2 m\(^3\)/s (6–12,000 L/min) and inlet pressures ranging from 2 bar to 45 bar.

From this data, specific cost information was derived by numerical interpolation in MATLAB. The interpolation used a Delaunay triangulation function of the operating pressure-ratio and inlet volumetric flow-rate (i.e., \( P_{hi}/P_{at} \) and \( V_i \)), and produced a piecewise-linear continuous surface passing through the supplied data points. The required expander costs at specific operating conditions were then linearly interpolated from this surface. A similar approach was used for the estimation of the pump costs.

3. Thermodynamic properties of working fluids with SAFT-VR Mie

3.1. SAFT equation of state

Most of the currently deployed heat engines utilize pure (single-component) fluids, hence the thermodynamic-property modeling of these engines has been historically focused on pure working fluids. Thermodynamic data for pure fluids can be reliably sought from sources such as the NIST/TRC Web Thermo Tables, which contain a wide range of experimental and pseudo-experimental thermodynamic properties for a large set of pure fluids. Experimental thermodynamic properties of fluid mixtures of potential interest, however, are frequently unavailable – particularly properties such as enthalpies, entropies and heat capacities, which are important in our current work; moreover, where they are available, the data are unlikely to represent the particular compositions of interest. Thus, in order to model fluid mixtures of arbitrary composition properly, a means of predicting the necessary thermodynamic information is required. For the purpose of ORCs, an approach to reliably and simultaneously predict both phase-equilibrium and calorific quantities is required.

Cubic equations of state (EoS), such as the Peng–Robinson [46] or the Soave–Redlich–Kwong [47], have been employed over the years for the modeling of phase-equilibrium properties, especially in the oil and gas, and petrochemical industries. These equations are, however, best suited for the prediction of phase-equilibrium properties in \( P-T-x \) space, and are less reliable for the prediction of calorific properties (heat capacities, enthalpies) for both pure fluids and fluid mixtures [48]. They are even less accurate for the calculation of second-derivative properties (e.g., coefficient of thermal expansion, isothermal compressibility). These shortcomings are not entirely unexpected as these EoS are semi-empirical in nature and their underlying molecular models (based on a hard spherical core surrounded by a spherically symmetric region of attraction) are usually not sufficiently realistic.

The development of molecular EoS such as the perturbed hard-chain theory (PHCT) and the associated perturbed anisotropic chain theory (APACT) EoS for chain molecules has provided some insight into addressing these deficiencies. Also, advances in statistical mechanics coupled with increased computational capabilities have led to the development of EoS based on molecular principles, which provide more realistic and accurate descriptions of real fluids and fluid mixtures. Foremost among these is arguably the statistical associating fluid theory (SAFT) EoS [49,50]. SAFT possesses a predictive capability lacked by cubic EoS, which it inherits from its firm theoretical foundation in statistical mechanics. This allows confidence in predictions of thermodynamic properties made outside the range of the experimental data used for the adjustment of the model parameters, and even in predictions of properties that were not considered in the process of model refinement.

The present study uses the SAFT-VR Mie EoS for the prediction of fluids’ thermodynamic properties. A thorough discussion of the adequacy of the SAFT-VR Mie EoS and its advantages compared with cubic EoS and previous versions of SAFT has been presented in the paper by Lafitte et al. [37]; in particular, it was shown that the SAFT-VR Mie EoS can be conveniently deployed to produce an accurate description of the thermodynamic properties of each of the classes of fluids considered in this present work – alkanes and perfluoroalkanes. For the specific details of the SAFT-VR Mie EoS the reader is referred to the original reference [37]; here we provide only a brief description. Similar to other versions of SAFT,
SAFT-VR Mie is a molecular-based EoS that allows the calculation of a fluid’s Helmholtz free energy, following the development of its underlying molecular model. The fluid molecules are modeled as chains of $m$ spherical segments that interact through a Mie (generalized Lennard–Jones) pair potential centered on each segment:

$$
\phi(r) = \frac{\lambda_s}{r_s - \lambda_a} \left( \frac{\lambda_a}{r_s} \right)^m \rho \left[ (\sigma)^m \right] \left( \frac{\sigma}{r} \right)^{\lambda_a}.
$$

(20)

Here, $r$ represents the separation of the two interacting segments, $\sigma$ is a parameter representing the size of the segment, $\epsilon$ is the depth of the potential well, and $\lambda_s$ and $\lambda_a$ are respectively the repulsive and attractive exponents characterizing the range of the potential; for the case $\lambda_s = 12$ and $\lambda_a = 6$, Eq. (22) reduces to the standard Lennard–Jones potential. Thus, the set of parameters comprising the model is divided into a sum of terms representing individual contributions due to: the monomer segments; the grouping of the chains of (of length $m$) that make up the model molecules; and (in the case of associating molecules) association. The generic SAFT free energy can thereby be written as:

$$
\alpha = a_\text{ideal} + a_\text{mono} + a_\text{chain} + a_\text{assoc}.
$$

(21)

In the current work we do not consider associating molecules, whereby $a_\text{assoc} = 0$. The ideal contribution, $a_\text{ideal}$, is calculated by providing the ideal-gas specific heat capacity $c_p^0$ for the fluid as a function of temperature. A standard approach is to correlate these using polynomials in temperature [51]; here we correlate ideal-gas heat capacities from the NIST database [26] using 3rd order polynomials. Then, $a_\text{ideal}$ is obtained via the integration of $c_p^0$ (to give the enthalpy) and of $c_p^0/T$ (to give the entropy). The coefficients of the polynomials for the working-fluid mixtures considered are listed in Table 1.

Once the Helmholtz free energy is defined, standard thermodynamic relations are used to derive thermodynamic properties of interest (e.g., pressure, fugacities, activity coefficients and chemical potentials). A particular feature of SAFT-VR is the facility to adjust $\lambda_s$ to suit the relative softness or hardness of a given molecule, allowing it to provide accurate descriptions of second-derivative properties, such as heat capacities, while maintaining a faithful representation of phase equilibrium [37]. An accurate description of these properties is particularly important in our current work, wherein one seeks to capture (for example) the thermal behavior of the specific entropy, which is closely related to the heat capacity.

Fluid mixtures are treated using van der Waals-one-fluid mixing with standard combining rules and no further adjustments (i.e., binary-interaction parameters are not employed), as per:

$$
\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}, \quad \Gamma_{ij} = \frac{1}{2} \left( \frac{\sigma_i}{\sigma_j} + \frac{\sigma_j}{\sigma_i} \right)
$$

(22)

For further details of mixture modeling the reader is directed to the Appendix of Ref. [37].

3.2. Alkane and perfluoralkane fluid models

Given the goal of demonstrating the predictive power of the proposed modeling approach, we consider fluorocarbon mixtures of n-perfluorobutane and n-perfluorodecane (n-C$_4$F$_{10}$ + n-C$_{10}$F$_{22}$) for which mixture data is not available in the literature. The results are compared with those of alkane mixtures of n-butane and n-decane (n-C$_4$H$_{10}$ + n-C$_{10}$H$_{22}$), which are corresponding analogue substances that are particularly well-suited fluids for validating the SAFT-VR Mie approach. Firstly, alkanes are common ORC working fluids [8,10,12–14] and, beneficially, extensive experimental property data are readily available for pure butane and decane, as well as for their mixtures. Alkanes are also non-associating molecules, so they present a useful starting point before proceeding to molecules with higher levels of complexity. Another reason for using the alkanes as a basis for comparison is that they were also considered in Ref. [5] albeit in an application with a different condensing condition and at a smaller scale (<4 MW). It is noted that the ORC systems presented in this paper are an order of magnitude larger in terms of power output (up to 30 MW; see Figs. 7 or 10). This, together with the different conditions imposed in the condenser, lead here to conclusions concerning ORC system cost and performance (e.g., see Fig. 11(c) for the alkane mixtures) that are in direct opposition to those in Ref. [5] (i.e., Fig. 11 in Ref. [5] for the same mixtures), necessitating revised ORC simulations with the alkanes for a suitable comparison.

The models for the alkanes and n-C$_4$F$_{10}$ are already available [37]; here we develop a new model for n-C$_{10}$F$_{22}$. Model parameters are obtained by adjustment to provide the best description of experimental vapour pressures $P_{\text{exp}}$ and saturated-liquid densities $\rho_{\text{sat}}$, as well as single-phase densities $\rho$ (both of the condensed and the superheated-liquid), and the speed of sound $u$. In particular, the following least-squares objective function, comprising the sum of the residuals from each of the considered properties, is minimized:

$$
\min_\theta M = \frac{W_p}{N_p} \sum_{i=1}^{N_p} \left( \frac{P_{\text{exp}}^i(T_i)}{P_{\text{sat}}^i(T_i)} - \frac{P_{\text{calc}}^i(T_i)}{\rho_{\text{sat}}^i(T_i)} \right)^2 + \frac{W_p}{N_p} \sum_{i=1}^{N_p} \left( \frac{\rho_{\text{exp}}^i(T_i)}{\rho_{\text{calc}}^i(T_i)} \right)^2 + \frac{W_p}{N_p} \sum_{i=1}^{N_p} \left( \frac{u_{\text{exp}}^i(T_i)}{u_{\text{calc}}^i(T_i)} \right)^2
$$

(23)

Here, $\theta$ represents the vector of parameters of the intermolecular model; the $N_p$ are the numbers of experimental data points; the superscripts ‘exp’ and ‘calc’ refer to experimental data points and calculated values respectively. The $W_p$ are weights attached to each property residual; here all properties are assigned equal weight $w_j = 1$.

The thermodynamic conditions considered for the experimental data are provided in Table 2; these were chosen to maintain relevance to the typical operation of an organic Rankine cycle. The resulting intermolecular parameters resulting from the optimization of the objective function ($M$) are presented in Table 3.
are used for the modeling of the fluids. The corresponding percentage average absolute deviation AAD (%) of the theoretical calculations from the experimental data for the investigated pure-fluid properties are presented in Table 4. The AAD (%) is computed as:

$$\text{AAD} = \frac{1}{N_p} \sum_{i=1}^{N_p} \left| \frac{X_{i}^{\text{exp}} - X_{i}^{\text{calc}}}{X_{i}^{\text{exp}}} \right| \times 100.$$  

where $X_{i}^{\text{exp}}$ and $X_{i}^{\text{calc}}$ are the experimental and computed properties respectively, and $N_p$ is the number of experimental data points used in the calculation.

It is noted from the results that the overall deviations are generally low for vapour–liquid equilibria and second-derivative thermodynamic properties. The deviations from the critical temperature and pressure are also low, although not of great importance in our current study (in which we focus on the sub-critical region) this is particularly gratifying as such good descriptions of both critical and sub-critical regions are, generally, difficult to obtain simultaneously, and will prove useful in future work.

### 3.3. Validation of SAFT models with experimental data

The effectiveness of the SAFT-VR Mie modeling approach in predicting the thermodynamic properties and phase behavior of the $n$-C$_{10}$F$_{22}$ and $n$-C$_{10}$F$_{10}$ + $n$-C$_{10}$F$_{22}$ systems is illustrated in Figs. 2–5. In practice, thermodynamic cycles such as ORCs are analyzed using diagrams in $T$–$s$ or $P$–$h$ spaces, hence experimental data in these spaces would ideally be required for the validation of the SAFT approach. To the best of our knowledge, only pure-component (and not mixture) phase-equilibrium data are available for these systems in these representations. Moreover, we are not aware of any experimental data in any of the $P$–$x$, $T$–$x$ or $P$–$T$ spaces relating to the $n$-C$_{10}$F$_{10}$ + $n$-C$_{10}$F$_{22}$ mixture system.

#### 3.3.1. Thermodynamic properties of pure working fluids

The vapour–liquid temperature–density ($T$–$q$) coexistence envelope for $n$-perfluorobutane calculated with SAFT-VR Mie are presented in Fig. 2(a). Also included are density isobars (at $P = 2$, 5, 20 and 40 bar). In this (and subsequent figures) symbols represent experimental data (here taken from the NIST Web thermodynamic tables [52]), while curves represent calculations. Similarly, the $T$–$q$ coexistence envelope for $n$-perfluorodecane and its superheated-vapour isobars are plotted in Fig. 2(c); note that experimental data are available only for the isobars between 1 bar and 4 bar. The description of the fluid density in all the regions of interest – the sub-critical condensed-liquid and superheated-vapour phases as well as the supercritical region – is excellent. This degree of agreement is extremely challenging to achieve using an analytical EoS, and we are not aware of any literature where a similar degree of agreement has been reported. It is well known that fluorinated hydrocarbons are difficult to describe with traditional intermolecular potentials, due partly to their high polarizability and the repulsive nature of the electronegative fluorines in the molecules [53].

The specific heat capacities of perfluorobutane as functions of temperature are shown in Fig. 2(b). The four isobars ($P = 2$, 5, 20 and 40 bar) have similarly been chosen to span both sub-critical and supercritical regions and both condensed-liquid and superheated-vapour regions. Although slight deviations are recorded close to the critical region, once again the descriptions obtained with the SAFT-VR Mie EoS are in very good agreement with the available experimental data; this highlights the predictive power of the EoS (since these data were not included in the refinement of the model parameters). Experimental data relating to the specific heat capacity of perfluorodecane are available only for the saturated-liquid phase. These have been plotted along with the calculations obtained by SAFT-VR Mie in Fig. 2(d). Once again, the calculations are in good agreement with the available experimental data.

In Fig. 3 we present similar thermophysical properties of the alkane analogues—$n$-butane and $n$-decane. Here, the isobaric specific heat capacities and densities (including the vapour–liquid saturation densities) calculated with SAFT-VR Mie are substantiated with experimental data from NIST. The descriptions of these pure-fluid properties provided by SAFT-VR Mie are seen to be consistent with the experimental data. It is clear from Figs. 2 and 3 that SAFT-VR Mie provides an excellent description of the thermodynamic properties of each of the four pure components considered in our study.

---

**Table 2**

Pressure and temperature ranges of the experimental data considered in the determination of average absolute deviation AAD (%) given in Table 3. Experimental data points are taken from the NIST Web thermodynamic tables [52]; the number of experimental data points used for each evaluation is given in parentheses.

| Fluid | VLE | Single-phase properties (compressed liquid and superheated vapour) |
|-------|-----|---------------------------------------------------------------|
|       | $T$ range/°C | $P$ sat/bar | $\rho$ | $q$ | $\rho$ | $q$ | $P$ range/bar |
| $n$-C$_4$H$_{10}$ | -40 to 150 (39) | -40 to 150 (39) | -40 to 150 (819) | -40 to 150 (819) | -40 to 150 (819) | 1 to 50 | 1 to 50 | 1 to 50 |
| $n$-C$_4$H$_{12}$ | 0 to 320 (66) | 0 to 320 (66) | 0 to 320 (1576) | 0 to 320 (1576) | 0 to 320 (1576) | 1 to 50 | 1 to 50 | 1 to 50 |
| $n$-C$_{10}$F$_{10}$ | -40 to 120 (32) | -40 to 120 (32) | -40 to 120 (741) | -40 to 120 (741) | -40 to 120 (741) | 1 to 50 | 1 to 50 | 1 to 50 |
| $n$-C$_{10}$F$_{22}$ | 0 to 270 (56) | 0 to 250 (52) | 50 to 260 (1035) | 50 to 260 (1035) | 50 to 260 (1035) | 30 to 260 (46) | 0.1 to 5.2 | 0.2 to 12 |

**Table 3**

Model parameter values for the pure compounds estimated from experimental single phase and phase equilibrium data using the SAFT-VR Mie EoS. Values for the alkanes and $n$-C$_4$F$_{10}$ are taken from Ref. [37]. Values for $n$-C$_{10}$F$_{10}$ are generated in this work starting from the same $\lambda$ value (5.7506) as that of $n$-C$_4$F$_{10}$ and tuning $\lambda_i$ to best match experimental data.

| Fluid | $m$ | $\sigma$/Å | $\epsilon$/kK | $\lambda$ | $\lambda_0$ |
|-------|-----|-------------|----------------|----------|-----------|
| $n$-C$_4$H$_{10}$ | 1.8514 | 4.0887 | 273.64 | 13.650 | 6.0 |
| $n$-C$_4$H$_{12}$ | 2.9976 | 4.5890 | 400.79 | 18.885 | 6.0 |
| $n$-C$_{10}$F$_{10}$ | 2.1983 | 4.4495 | 290.49 | 24.761 | 5.7506 |
| $n$-C$_{10}$F$_{22}$ | 2.8693 | 5.2281 | 382.63 | 26.508 | 5.7506 |

**Table 4**

Average absolute deviation AAD (%) from experimental values of selected thermodynamic properties and phase behavior of the alkanes and tuning $\lambda_i$ to best match experimental data.

| Fluid | m | $\sigma$/Å | $\epsilon$/kK | $\lambda$ | $\lambda_0$ |
|-------|-----|-------------|----------------|----------|-----------|
| $n$-C$_4$H$_{10}$ | 0.38 | 0.74 | 0.37 | 4.19 | 1.52 | 1.73 | 0.22 |
| $n$-C$_4$H$_{12}$ | 0.80 | 0.68 | 0.78 | 2.55 | 0.46 | 1.40 | 2.14 |
| $n$-C$_{10}$F$_{10}$ | 0.57 | 1.75 | 1.99 | 6.69 | 0.78 | 0.29 | 0.79 |
| $n$-C$_{10}$F$_{22}$ | 0.60 | 1.56 | 1.94 | 4.60 | 0.09 | 4.07 |

are consistent with the experimental data. It is clear from Figs. 2 and 3 that SAFT-VR Mie provides an excellent description of the thermodynamic properties of each of the four pure components considered in our study.
3.3.2. Thermodynamic properties of binary-mixture working fluids

First, we provide the SAFT-VR Mie description of the alkane mixtures \((n\text{-C}_4\text{H}_{10} + n\text{-C}_{10}\text{H}_{22})\) in \(P-T-x\) space; for comparison, we also provide this experimental data available in these spaces. Presented in Fig. 4(a) are the \(P-T\) vapour–pressure curves for \(n\)-butane \((x_{\text{C}_4\text{H}_{10}} = 1)\) and \(n\)-decane \((x_{\text{C}_{10}\text{H}_{22}} = 0)\) calculated with SAFT-VR Mie, interspersed with constant–composition \(P-T\) bubble-point curves of their mixtures. The dew-point curves have been omitted to give clarity to the figure. Experimental data from three sources – the NIST database, corresponding pure-component experimental data are also provided for comparison. To the best knowledge of the authors, mixture data for these fluids are unavailable at present. The SAFT-VR Mie calculations provide a very good representation of the pure-component phase equilibria in this space. Although there are no experimental data to validate the \(P-T\) envelopes of the perfluoroalkane mixtures, one can visually discern (from Fig. 4(a)) that the plotted envelopes follow a similar trend to that seen for the alkane mixtures, which was substantiated by experimental data. We are therefore confident that the vapour–liquid predictions for the perfluoroalkane mixtures provided by SAFT-VR Mie conform to the same degree of accuracy as the description of their alkane analogues.

We conclude this section by verifying the ability of SAFT-VR Mie in predicting the phase equilibria of the alkane mixtures and their perfluoroalkane analogues in \(T-s\) and \(P-h\) spaces, which are crucial for the purposes of the thermodynamic analyses required in the present study. In Fig. 5(a), predicted phase envelopes for both pure \(n\)-perfluorobutane and pure \(n\)-perfluorodecane are presented in \(T-s\) space, together with those of intermediate mixtures comprising 30 mol%, 60 mol%, 80 mol% and 90 mol% \(n\)-perfluorobutane and \(n\)-perfluorodecane in order to illustrate the crossover in the phase behavior between the two pure components. Also provided are the experimental phase-envelopes for each of the pure components (from the NIST database), as indicated by the symbols. These phase envelopes are also provided in \(P-h\) space (for both pure fluids, 30 mol%,
Fig. 3. Selected thermodynamic properties of n-butane and n-decane: (a) vapour–liquid T–P coexistence envelopes and density isobars (at indicated pressures) for n-butane; (b) temperature dependence of the isobaric heat capacity \( c_p \) of n-butane; (c) vapour–liquid T–P coexistence envelopes and density isobars for n-decane; and (d) temperature dependence of the isobaric heat capacity \( c_p \) of n-decane. Comparison of experimental data from NIST (symbols) with the description obtained using SAFT-VR Mie EoS (continuous curves).

50 mol% and 80 mol% n-perfluorobutane) in Fig. 5(b), once again incorporating experimental pure-component data from NIST. (N. B.: The reference state for the data in Fig. 5 is defined by \( h = 0 \) and \( s = 0 \) at the saturated-liquid temperature \( T = 273.16 \text{ K} \)). The phase envelopes (both calculated and experimental in T–s and P–h) of n-butane, n-decane and their mixtures are also provided in Fig. 5(c) and (d). The agreement between the calculated and experimental pure-component phase envelopes in these figures is very promising, especially when one takes into account that these experimental data were not considered during the refinement of the molecular model parameters \( m, \sigma, \kappa, \xi_s \), and \( \lambda_s \).

Overall, the quality and consistency of agreement between the SAFT-VR Mie predictions and the experimental data for the pure components illustrated in Figs. 2–5 emphasizes the predictive power of the proposed modeling approach, and provides confidence in the reliability of the thermodynamic-property predictions for the mixtures (for which the analogous experimental P–h and T–s phase envelopes are not readily available). Furthermore, the predictive performance of the approach for the alkane mixtures in P–T space is considered excellent, as is the performance for the same fluids in the P–h and T–s spaces. Unfortunately, as stated earlier, carrying out the same validation for the perfluoroalkane mixtures is not possible due to the lack of experimental data. Nevertheless, given that the perfluoroalkanes are structural analogues of the well-validated alkanes and the similarity exhibited in the results of the two chemical classes throughout Figs. 2–5, the results suggest that the predictions of the required thermodynamic data of the perfluoroalkane mixtures will also be appropriate. One of the primary purposes of this study is to provide a method by which predictions of working-fluid properties (pure and mixtures), especially in the T–s and P–h spaces, can be made with relative reliability, even in the absence of experimental data. In summary, the results in this section give confidence that this is the case, at least for the classes of chemical compounds that were considered here as working fluids.

4. ORC simulation results

Using the above-mentioned SAFT approach, the thermodynamic properties (heat capacities, enthalpies, entropies, densities, etc.) of a range of working fluids were generated in P–T–x space. These were stored in lookup tables and accessed by the ORC model via interpolation. The investigated ranges of the variables of interest are listed in Table 5. These were varied between the stated lower and upper bounds in order to reveal their effect on the performance and cost indicators of the ORC engines under consideration.

In Figs. 6–8, we present results for the specific power output \( W/\text{th} \), absolute (net) power output \( W \), and the thermal efficiency \( \eta_{\text{th}} \), as functions of the butane and perfluorobutane mole fractions in the n-butane + n-decane and n-perfluorobutane + n-perfluorodecane working-fluid mixtures, for evaporating pressures ranging from 6 bar to 40 bar. For the cases where the evaporating pressure exceeds 90% of the critical pressure of the corresponding working fluid, the simulation results are omitted, thus focusing the present work to sub-critical cycles. In general, the overall trends are similar between the alkanes and their perfluoroalkane analogues. However, the critical pressures of the
perfluoroalkanes are lower than the alkanes, therefore only evaporation pressures \( P_{23} \) up to 22 bar are considered for the perfluoroalkanes.

Condensing the working fluid at the lowest possible pressure and temperature is desirable from the point of view of increasing the work extracted from the cycle. Now, given that the inlet temperature of the cooling stream is 20 °C, and that the prescribed minimum pinch temperature difference is 10 °C, the temperature of the working fluid at State 1 must be at least 30 °C (or higher for finite cooling-stream flow-rates for which the cooling-stream temperature increases through the condenser). In addition, we specify that the cycle should be operated at above atmospheric pressures in order to allow an affordable system design; sub-atmospheric pressures require complex designs to prevent air ingress into the engine that act to increase the costs of the system. Thus, the cycles are also designed such that the lowest cycle pressure (condensation pressure \( P_{\text{c}} \)) is at least 1 bar (or higher).

Mathematically, the above two restrictions on the condensation pressure and temperature can be summarized as: \( T_1 = T_{\text{bub}}(P_{\text{c}}) > 30 °C \) and \( P_{\text{c}} = P_1 = \max\{1 \text{ bar}, P_{\text{sat}}(T_1)\} \). Sections 4.1 to 4.3 deal with the idealized case of infinite cooling flow-rates through the condenser and, thus, constant condensation temperatures, for which \( T_1 = \max\{30 °C, T_{\text{bub}}(1 \text{ bar})\} \) and \( P_{\text{c}} = P_1 = \max\{1 \text{ bar}, P_{\text{sat}}(30 °C)\} \); finite cooling flow-rates are considered in Section 4.4.

It can be seen from Figs. 6–8 that mixtures with low mole fractions of \( n \)-butane/perfluorobutane (high decane/perfluorodecane content) have sub-atmospheric bubble-point pressures at the desired condensation temperature at the condenser outlet. Therefore, for \( n \)-butane mole fractions below 30 mol% and perfluorobutane mole fractions below 20 mol%, the condensation pressure \( P_{\text{c}} = P_1 = P_4 \) is set to 1 bar and the condensation temperature at the condenser exit \( T_1 \) is equal to the saturation temperature at the condensing pressure, \( T_{\text{bub}}(P_{\text{c}} = 1 \text{ bar}) > 30 °C \). Accordingly, two regimes can be distinguished in the figures for the regions below (Regime I) and above (Regime II) 30 mol% of butane or 20 mol% perfluorobutane in the mixtures. In Regime I, the pressure through the condenser is set to \( P_{\text{c}} = 1 \text{ bar} \) (and the condenser outlet temperature is above 30 °C), whereas in Regime II it is set to the saturation pressure corresponding to the condenser outlet temperature when this is set to \( T_1 = 30 °C, P_{\text{c}} = P_{\text{sat}}(T_1 = 30 °C) \) (and is above 1 bar). For the purpose of comparison, corresponding results for when the mixture is permitted to expand below 1 bar to reach a condenser outlet temperature of 30 °C, or \( P_{\text{c}} = P_{\text{sat}}(T_1 = 30 °C) < 1 \text{ bar} \), are also shown in these figures at low butane/perfluorobutane mole fractions, represented by dotted lines.

4.1. Power output

To maximize the mass-specific power output (\( W/m \)) it is found (from Fig. 6) that the optimal working fluid in a non-superheated case is a mixture comprising of 30 mol% butane or 20 mol% perfluorobutane. It is also found that superheating increases the specific power output, in agreement with other studies, due to the higher specific enthalpy change through the expander. If the working fluid is superheated to the maximum degree allowed by the heat-source stream \( (i.e., \Delta h_{\text{sh}} = 1) \), pure butane and pure perfluorobutane emerge as the optimal working fluids. Perfluoroalkane mixtures exhibit the same general behavior as their alkane counterparts, however, the specific power outputs are much lower by a factor of about 4–5, because the heat capacities of the alkanes are much higher than those of the perfluoroalkanes.

For the \( n \)-butane + \( n \)-decane working-fluid mixtures, \( W/m \) generally decreases with increasing butane content, especially at low evaporation pressures. This is a direct result of pure butane having a lower specific heat capacity and, in turn, a lower specific enthalpy difference between State 3 and State 4, \( h_3 - h_4 \), compared to decane. Also, the mixtures with higher butane content have higher dew-point pressures at 30 °C and are thus expanded to higher pressures, thereby producing lower power outputs. In cases where the mixtures with high decane content are expanded to the dew-point pressures at 30 °C (i.e., below 1 bar, as depicted with the dotted lines in Fig. 6), we see a monotonically decreasing trend of the
specific power output with the increasing butane mole fraction, with pure decane (due to its very low saturation pressure of 0.0026 bar) producing the highest specific power output and pure butane producing the least. However, since in Regime I the condensing pressure is set to 1 bar (which, for instance, is equivalent to a condensing temperature of 173 °C for pure decane), the difference in specific enthalpy difference \( h_{\text{n}} \) is reduced considerably.

Specific power is a valuable and commonly used performance indicator in cycle analysis since it is an output that depends only on the thermodynamic properties around the cycle and not the working-fluid or external heat source/sink stream mass flow-rates (and hence the system size), thus decoupling and highlighting information relating to the cycle. It is not however a sufficient figure-of-merit for the associated ORC plants. If maximizing power output is a chief aim, specific power can be misleading in choosing a suitable cycle and working fluid [4,5]. A more appropriate measure is the maximum net power output. This includes information on the working-fluid flow rate that can be calculated directly for a given cycle and mixture by increasing the working-fluid flow rate until the pinch condition is met.

The net power output \( (W) \) is plotted for non-superheated and superheated cycles \( (d_{\text{SH}} = 1) \) for alkanes and perfluoroalkanes in Fig. 7(a–d). In addition, the maximum power outputs obtained for a given mixture over all degrees of superheating are plotted in Fig. 7(e) and (f). The power outputs of the perfluoroalkanes are distinctly lower than the alkanes, although the trends are mainly the same. These plots clearly indicate that the non-superheated cycles produce higher power outputs than the superheated ones, contrary to the results suggested by the specific power outputs. Furthermore, Fig. 7(a) and (c) are virtually identical to Fig. 7(e) and (f), respectively (only a few points are different, and then only slightly), which suggests that cycles optimized for maximum power output should not be superheated. The 30 mol% butane and 20 mol% perfluorobutane mixtures are the optimal working fluids for very low evaporation pressures up to 6 bar. In Regime II, the net power produced is approximately constant at low evaporation pressures, but it increases monotonically with the \( n \)-butane/perfluorobutane mole fraction at higher evaporation pressures. The highest power output is achieved at the higher evaporation pressures by pure \( n \)-butane/perfluorobutane.

### 4.2. Thermal efficiency

The thermal efficiencies of the investigated cycles corresponding to Figs. 6 and 7 are plotted in Fig. 8. For low evaporation pressures, the higher-molecular-weight fluids (\( n \)-decane/ perfluorodecane) result in the highest efficiencies (in both regimes) whereas at higher pressures pure \( n \)-butane/perfluorobutane...
produce the maximum efficiencies. This is the general behavior for non-superheated and superheated cycles. In summary, one should avoid mixtures to maximize efficiency in the chosen case study.

It is interesting that superheated cycles tend to be less efficient, which may seem counterintuitive given that the average temperatures of heat addition and the maximum cycle temperatures are higher in these cycles. To understand this, one must also consider the heat-rejection process, whose average temperature is also increased, and even more so because n-decane/perfluorodecane are drier fluids than n-butane/perfluorobutane, as illustrated in the T–s diagrams in Fig. 5. The dryness of the working fluid increases with the proportion of n-decane/perfluorodecane in the working-fluid mixture, whereby the vapour entering the condenser is increasingly superheated, adversely affecting the thermal efficiency. This also suggests that for wet fluids it can be the case that superheating may increase efficiency. At higher evaporating pressures (closer to the critical point), the decrease in efficiency with superheating is less pronounced. In comparison to alkanes, the thermal efficiencies when using mixed perfluoroalkanes are slightly lower (by about 1–2%). This is in part due to their lower heat capacities and enthalpies of vaporization.

As stated earlier, because the cost of waste heat as a resource is far smaller in comparison to, e.g., conventional fossil-fueled plants, power output is favored over thermal efficiency as a figure-of-merit in waste-heat conversion applications. Notably, thermal efficiency and power output do not necessarily give similar indications for optimal performance. When operating with practical heat sources or sinks whose temperatures change (as opposed to constant-temperature heat-reservoirs), a rising efficiency often leads to a decrease in power output [59]. We have observed this for 10 mol% butane–decane mixtures. The maximum-power-output cycle at 16 bar has a lower power output than its 4 bar and 10 bar counterparts, however, the thermal efficiency is higher. A rise in power output (by increasing mass flow-rate or evaporation pressure) from a certain point, leads to a decrease in the inlet temperature of the evaporator lest the pinch condition be violated. This leads to an overall reduction of the efficiency. Therefore, a maximum efficiency does not necessarily mean that the cycle extracts the maximum possible amount of heat from the heat source, which may lead to a penalization in power output.

The previous observations suggest that pure butane is generally associated with higher efficiencies and power outputs than its mixtures. This finding is in contrast to several results in the literature, as mentioned in the introduction. Fluid mixtures allow an increase in the average temperature of heat addition without violating the pinch condition, thereby introducing the potential for increasing efficiency. However, deploying fluid mixtures also increases the average temperature of heat rejection leading to an efficiency and power-output penalty. This is illustrated in Fig. 9. The diagram on the left is a cycle using pure butane; the one on the right is a cycle with a 50 mol% butane mixture. The enclosed area of the cycles is a measure of the net work output of the cycle. Additionally, the ratio of the area enclosed by the cycle to the area below the heat-addition process is a measure of the thermal efficiency. From Fig. 9 it can be seen that the non-isothermal heat-rejection process of the mixture cycle reduces the enclosed area in comparison to the pure-fluid cycle, which explains the reduction in the power output and efficiency for mixtures.

We note here that in conventional power generation, including waste-heat conversion with sufficient and affordable access to...
cooling water, a fluid mixture would be sought that exhibits the optimal temperature glide during evaporation and that exhibits near azeotropic behavior at the condensation conditions. In general however, and especially for ORC systems aimed at energy integration and combined heat and power, optimal plants will (by design) require a balancing of what may be significant glides in both evaporator and condenser.

4.3. Cost comparisons

4.3.1. Variation of ORC costs with power output

The costs of the ORC systems investigated previously are presented in Fig. 10. The total cost presented in this figure is the summation of the costs associated with the purchase of the four main components of the cycle, i.e., the working-fluid pump, the evaporator, the expander and the condenser. Although this is adequate for comparison purposes, it should be noted that the actual installation costs of ORC engines would be higher than those portrayed in this figure. The costs for ORCs with the perfluoroalkanes as working fluids show the same trends as that present in Fig. 10 for the alkanes; they have thus been omitted.

From Fig. 10 it is clear that the cost of ORC systems is strongly correlated with power output. For small- and medium-scale systems up to 100 kW, the total cost of the systems increases from about £8,000 for the smallest system (0.2 kW) to £30,000–£50,000 for the largest ones in this system-size range (100 kW), while the cost per unit power output drops steeply from £40,000 to £300–£500 per kW, respectively. As a limited form of support for the cost values in Fig. 10, the CEP Laboratory where the authors are based has an operational ORC system rated to 1 kW whose cooling water, a fluid mixture would be sought that exhibits the optimal temperature glide during evaporation and that exhibits near azeotropic behavior at the condensation conditions. In general however, and especially for ORC systems aimed at energy integration and combined heat and power, optimal plants will (by design) require a balancing of what may be significant glides in both evaporator and condenser.
construction costed approximately £7,000, or £7,000 per kW. These values fall close enough, for the purposes of the present effort, to the £10,000 and £10,000 per kW cost estimates indicated in Fig. 10. As expected, a 100 kW system should be a more economically viable solution when payback period is a significant factor and the investor is able to accept the higher capital costs.

For large-scale ORC systems (100 kW–30 MW), the total costs appear roughly proportional to the power output and the costs per unit power remain fairly constant between £150 and £500 per kW. The increase in total costs is a direct result of the large working-fluid mass flow-rates required, which necessitates the use of large turbines and heat exchangers. The costs of the turbines appear as the most dominant among the individual component costs, and since these scale with power output, the total costs of the systems follow the same trend.

4.3.2. Effect of working-fluid mixtures on ORC system costs

To compare ORC system costs when employing working fluids with different mixture compositions, the total costs of systems designed for maximum power output are presented in Fig. 11 both in total cost (£), and in specific cost per kW (£/kW). The corresponding maximum power outputs from these cycles are

![Graphs showing efficiency and temperature comparisons](image)

**Fig. 8.** Thermal efficiency $\eta_{th}$ of: (a) non-superheated cycles ($d_{SH} = 0$), and (b) maximum superheated cycles ($d_{SH} = 1$) as functions of $n$-butane mole fraction $x_{C4H10}$; (c) non-superheated cycles ($d_{SH} = 0$), and (d) maximum superheated cycles ($d_{SH} = 1$) as functions of perfluorobutane mole fraction $x_{C4F10}$.

![Graphs showing temperature and specific entropy comparisons](image)

**Fig. 9.** Pure butane cycle (left) and equivalent cycle of 50 mol% butane–decane mixture (right) in $T – s$ space. Also shown are the saturation curves of the corresponding working fluids.
given in Fig. 7(e) and (f) for the alkane and perfluoroalkane mixtures respectively. The total costs are generally not strongly affected by the butane/perfluorobutane mole fraction, except at higher evaporation pressures when they are higher. A noticeable feature (maximum) occurs for alkane mixtures at high pressures where the costs peak at butane mole fractions between 0.7 and 0.8.

The changes in costs per unit power output with the butane or perfluorobutane mole fraction are shown in Fig. 11(c) and (d). It can be seen that, when cycle data exist within the selected envelope of investigated conditions (Table 5), the pure fluids tend to be more cost effective than the mixtures. On the one hand, pure butane/perfluorobutane appear as the most cost effective options (in terms of £/kW) even though they are associated with high total costs because these fluids present the cycles with the highest maximum power outputs. On the other hand, pure decane/perfluorodecane cycles, while producing the least power output, have lower

Fig. 10. Performance (power output) and cost of ORC systems in the investigated case study. (a) Overall costs of the cycle against the power output for alkane mixtures. (b) Costs per unit power output against the power output for alkane mixtures. The colour range in all plots reflects the thermal efficiency of different cycles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 11. ORC system costs for systems designed for maximum power output. Total cost (£) with: (a) n-butane + n-decane, and (b) n-perfluorobutane + n-perfluorodecane working-fluid mixtures. Cost per unit power output (£/kW) with: (c) n-butane + n-decane (corresponding power output in Fig. 7(e)), and (d) n-perfluorobutane + n-perfluorodecane working-fluid mixtures (corresponding power output in Fig. 7(f)).
costs (in £/kW) than the intermediate mixtures at the same evaporating pressures. These results indicate that the pure working fluids considered in this work are, once again, more cost effective than the working-fluid mixtures. The use of higher evaporation pressures with pure butane/perfluorobutane increases the power output and cost by a similar extent, leading to a similar cost per unit power of ~£400/kW except at very low pressures (<10 bar).

4.4. Constrained cooling flows

In the previous sections, we considered ORC system performance and cost results for an idealized case in which, aiming to extract the maximum possible power, the cooling flow-rate is high enough that the cooling-stream temperature is constant through the condenser. Typically, one increases the working-fluid flow-rate and/or the evaporation pressure, while using a sufficient amount of cooling resource to ensure that the working fluid is fully condensed and that there is no pinch violation in the condenser. A large availability of cooling water is common in large-scale power-generation applications (e.g., power stations), where sufficient resources (e.g., from rivers and cooling towers) are made available from the early stages of a project.

For this case, the more-volatile pure working-fluid is seen to give better performance than the working-fluid mixtures. As stated earlier, this is influenced by the better thermal match between the cooling stream and the condensing pure working-fluid (e.g., see T–s diagram in Fig. 9). This conclusion is contrary to what is generally obtained from ORC studies in the literature where a working-fluid mixture maximizes the ORC power output over the constituent pure fluids. It should however be noted that the cooling resources considered in these studies were limited, wherein both the inlet and outlet temperatures of the cooling stream are specified (e.g., see Refs. [8,13,14]). This specification allows the working-fluid mixtures to be condensed at lower pressures by providing a temperature glide (and a closer thermal match) to the heat sink while the pure fluids are condensed at higher pressures to satisfy the pinch conditions caused by isothermal condensation profile. As such, the working-fluid mixtures can provide higher power output than the pure components.

Scenarios with limited cooling resources are often realized in practical applications, as highlighted in the Introduction, and include power generation in remote and/or arid areas, air-condensation with the aid of cooling fans, and CHP applications in which the ORC engine cooling-water is used for household/district heating. For the latter application in particular, the cooling water needs to be raised from ambient temperature to temperatures close to the boiling point, e.g., 90 °C [60–62], to mitigate against heat losses in the transport pipe networks. Such a constrained cooling requirement presents a case for which non-azeotropic working-fluid mixtures could be deployed to a great advantage. Results from such a case (with cooling water outlet temperature of 90 °C) are shown in Fig. 12, where the absolute power output and the temperature glides in the evaporator/condenser are plotted as functions of the n-butane mole fraction in the n-butane + n-decane working-fluid mixtures.

By comparison with Fig. 7(e), the ORCs with constrained cooling produce lower power output, especially with working fluids with high butane content. For working fluids with low butane content (high decane content), the maximum power output is similar in both constrained and unconstrained cases (Figs. 12(a) and 7(e), respectively) because the working fluids are condensed predominantly at 1 bar. However, for the working fluids with high butane content, the maximum power is much lower as the working fluids are condensed at the higher pressures imposed in our present approach. This is especially pronounced for pure butane where there is a decrease in power output of over 60% between the

![Graphs showing performance of ORCs with constrained cooling](image-url)
unconstrained cases and the constrained cases. This is primarily a result of the isothermal condensation profile that causes an increase in condensation pressure in response to the large temperature change in the cooling stream.

Overall, for the constrained cooling-flow cases investigated, the working-fluid mixtures lead to higher power outputs than both pure fluids as demonstrated in Fig. 12(a), with 50 mol% butane being optimal at low evaporation pressures and 80 mol% butane being optimal at higher evaporation pressures. The corresponding working-fluid evaporation and condensation temperature glides are given in Fig. 12(b). For the working-fluid mixtures large phase-change temperature glides are observed, up to ~130 °C in the in the evaporator and ~140 °C in the condenser. Such large temperature glides provided by the mixtures allow a better thermal match to the large temperature change required in the cooling stream (70 °C, from 20 °C to 90 °C). This leads to a decrease in the average temperature difference between the working-fluid mixtures and the cooling stream, a reduction of exergy losses in the condenser, and thus higher power outputs and thermal efficiencies (Fig. 12(c)) than the constituent pure fluids.

The specific ORC system costs (in £/kW) for the constrained cooling case are presented in Fig. 12(d). These, similar to the unconstrained case, show little variation between the pure fluids and the working-fluid mixtures with the exception of high butane-content cycles due to the significantly reduced power output from these cycles (see Fig. 12(a)).

5. Further discussion

The present study is aimed at assessing the potential of using fluorocarbon working-fluid mixtures in ORCs for low- to medium-grade heat conversion applications. Mixtures can provide an improved thermal match to the heat source and sink by exhibiting non-isothermal phase change behavior. This way, the average temperature differences (and associated exergy losses) during heat addition and rejection are minimized, which can lead to an enhancement of the power output and efficiency. To this end, sub-critical, non-regenerative ORCs using binary mixtures of fluorocarbons (n-perfluorobutane and n-perfluorodecanes) and alkanes (n-butane and n-decanes) were modeled with a view toward affordable, low complexity ORC plants. Values for the thermodynamic and phase-change properties of the mixtures for use in the thermodynamic cycle analyses were derived from the SAFT-VR Mie EoS. The choice of two dissimilar fluorocarbon (and alkane) components were selected because it is more challenging in terms of property prediction, but also in order to allow large temperature glides, which may be beneficial in certain ORC applications.

Another important aim of the research presented in this paper, therefore, was to assess the suitability of the SAFT-VR Mie equation of state for the provision of the thermodynamic properties of the working-fluid mixtures. The molecular basis of the equation and its firm foundation in statistical mechanics indicate that this approach could be an attractive alternative to those commonly used in the analysis of ORCs, such as REFPROP or CoolProp, for fluids that are not included in these databases, or for which significant uncertainties may be indicated. These software platforms employ correlative equations of state relying on the assignment of a large number of parameters, so the latter situation can arise, for example, when experimental thermodynamic-property data are scarce or restricted to narrow regions of phase space. Although one also requires experimental thermophysical-property data to parameterize the molecular models employed in the SAFT approach (typically vapour pressures and saturated-liquid densities are used), fewer parameters are used to represent a given fluid and, commensurately, fewer experimental data are required to obtain models that are reliable over large regions of the phase dia-

gram. Moreover, the parameters each have a clear physical meaning, whereby one can supplement these data with other information (such as the molecular size). Accordingly, an approach for modeling engineering cycles such as ORCs incorporating SAFT, complements nicely the more common method using REFPROP or CoolProp, and offers an appealing alternative.

The success of SAFT in modeling thermophysical properties in P–T–x space has been long established; as expected, the thermodynamic description of these fluids provided by SAFT-VR Mie in this space is excellent. However, one rarely encounters studies in which SAFT has been used to predict properties in T–s or P–h space; these spaces are of greater relevance in modeling engineering cycles, for which calorific quantities are of fundamental importance. It was particularly assuring, therefore, to find that the descriptions of the thermodynamics in these spaces were of equally high quality. Based on this, SAFT-VR Mie is clearly an appropriate tool for the provision of working-fluid thermodynamic information in the analysis of engineering cycles, such as ORCs.

Regarding the key thermodynamic performance indicators, such as the power output and the thermal efficiency, both sets of mixtures (alkanes and perfluoroalkanes) exhibit the same general behavior, at least for the application studied in the present work of a refinery flue-gas stream of a given duty as an example heat source at an initial temperature of 330 °C and a large cooling flow rate. Pure fluids result in higher thermal efficiencies than mixtures, with the heavier pure component (decane or perfluorodecane) being the most thermally efficient working fluid at low evaporation pressures and the lighter pure component (butane or perfluorobutane) being the most efficient at higher pressures. Generally, the uncovered relationships are non-trivial.

For applications such as waste-heat recovery and conversion, power output is a more useful indicator than the thermal efficiency, due to the fact the energy source (waste heat) is ‘nominally free’ and abundantly available. If one considers the maximum power output, which is our preferred indicator of performance, one is led to a pure working fluid; use of the pure lighter component (butane or perfluorobutane) clearly produces the highest power output in non-superheated as well as superheated cycles.

By taking these observations into consideration, we can infer that the optimal working fluid in this case study is the pure lighter component (butane or perfluorobutane) as its use produces the highest power output for almost all cases and exhibits the highest efficiency for evaporation pressures above 10 bar. Additionally, it also displays very low expansion ratios (not shown here). For low evaporation pressures, a low (perfluoro-)butane concentration (between 20 and 40 mol%) produces power outputs comparable to pure (perfluoro-)butane and the most efficient working fluid is pure (perfluoro-)butane. In conclusion, the overall performance of mixtures as working fluids was inferior to that of the pure substances; only under certain specific conditions was a mixture working fluid preferred.

Overall system costs tend to increase with the mole fraction of the low-molecular-weight component. This is, however, due to the increase of the power output, which correlates with the increase of the proportion of the aforementioned component. The cost per unit work output, tends to rise with the mole fraction before decreasing sharply for pure n-butane and perfluorobutane. In the present study, it is found that cycles based on pure substances from both ends of the molecular-weight scales are more cost-efficient than cycles running with mixtures. This conclusion may not apply in the case that a working-fluid mixture is formed from pure substances whose thermodynamic properties are more closely matched than was the case in the binary fluid-pairs investigated here.

A general conclusion from this work is that the choice of the optimum working fluid (pure or mixture) is sensitive to the
particular external heat source/sink conditions that the cycle is required to interface with thermally and, moreover, in non-trivial fashion that would be hard to expect intuitively. Although for the case study considered here, in which unconstrained quantities of cooling water are assumed to be available at zero cost, a working fluid comprising a pure component is to be preferred, this is not the case when significantly lower quantities of cooling water are available. Constraining the flow rate of cooling water was found to severely affect performance, whereby mixtures become the optimal working fluids; the precise composition depends on the cooling-stream temperature-rise and other cycle conditions such as the evaporation pressure. Consequently, in many applications it is important to consider the use of working-fluid mixtures, and in particular fluid mixtures with large glides, so that working-fluid design can be fully incorporated in the design of the cycle as a whole for the full range of applications of interest.

6. Conclusions and recommendations

This study highlights the capability of SAFT-VR Mie in predicting the thermodynamic properties of organic working fluids—pure substances and mixtures thereof—specifically with a view toward thermodynamic/thermoeconomic analyses of ORC systems. As a demonstration of its versatility, this molecular-based equation of state was shown to be able to deliver accurate caloric properties (in both $T$–$s$ and $P$–$h$ spaces) of alkanes and perfluoroalkanes, including those for which experimental data are scarce.

Based on the availability of the aforementioned thermodynamic data, ORC simulations revealed that in order to recover the maximum power output from a waste-heat source it is beneficial to limit the amount of superheating applied during the heat-addition process. Specifically, cycles without superheating, when the fluids are expanded from their saturated-vapour states without superheating, were observed to produce higher power outputs and also to be more efficient than cycles with superheating. Furthermore, cycles with the more-volatile pure working fluids (butane and perfluorobutane) were shown to deliver greater power, and were more efficient and cost effective than those featuring working-fluid mixtures. The lowest specific cost in the present case study was ~£400/kW for both of these pure fluids. The use of higher evaporation pressures with these fluids increased the power output and cost by a similar extent, leading to similar specific costs except at low pressures (<10 bar).

Working-fluid mixtures proved desirable in waste-heat-recovery applications with limited or constrained cooling resources as may be found in energy-intensive industries, arid regions and in combined heat-and-power applications. Their cycles were found to produce higher power outputs and were more efficient than those of pure working fluids. With such cooling streams, the condensation temperature glides of the working-fluid mixtures can be suitably optimized to provide an improved thermal match to the temperature profile of the cooling stream. Thus, unlike a pure fluid that would be limited by its isothermal condensation profile, fluid mixtures would be better suited for these applications.

While we have investigated the use of working-fluid mixtures from a thermodynamic point of view and made a first-order attempt to evaluate the cost of related systems, the heat-transfer characteristics of such mixtures are yet to be fully understood. In practice, it has been suggested that the heat-transfer coefficients deteriorate when using mixtures. The extent and effect of such variations on the size and cost of heat exchangers needs to be ascertained before ORC systems with mixtures can be implemented on a large scale. We would therefore recommend that thermal performance be more closely considered. Another practical consideration to bear in mind is the fractionation of working-fluid mixtures in the cycle due to the tendency of the heavier phase to separate. Thus, the engine and its components should be designed to ensure a continuous mixed phase. The ORC engine performance can be further improved by considering additional cycle architectures such as transcritical cycles, multiple evaporation cycles and cycles with internal regeneration.

Acknowledgment

This research was performed under the UNIHEAT project. The authors wish to acknowledge the Skolkovo Foundation and BP for financial support.

References

[1] Ammar Y, Joyce S, Norman R, Wang Y, Roskilly AP. Low grade thermal energy sources and uses from the process industry in the UK. Appl Energy 2012;89 (1):3–20.
[2] Markides CN. The role of pumped and waste heat technologies in a high-efficiency sustainable energy future for the UK. Appl Therm Eng 2013;53:197–209.
[3] Element Energy, Ecolys, Imperial College, Stevenson P (Larksdown Environmental Services), Hyde R (RHEnergy). The potential for recovering and using surplus heat from industry. Final report, department of energy and climate change. <https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/294900/element_energy_et_al_potential_for_recycling_and_using_surplus_heat_from_industry.pdf>; 2014.
[4] Aostoli M, Romano MC, Bombarda P, Macchi E. Binary ORC (organic Rankine cycles) power plants for the exploitation of medium–low temperature geothermal sources – Part A: Thermodynamic optimization. Energy 2014;66:423–34.
[5] Oyewummi OA, Taleb AI, Haslam AJ, Markides CN. An assessment of working-fluid mixtures using SAFT-VR Mie for use in organic Rankine cycle systems for waste-heat recovery. Comput Therm Sci 2014;6(4):301–16.
[6] Wang EH, Zhang HC, Fan BY, Ouyang MG, Zhao Y, Mu QH. Study of working fluid selection of organic Rankine cycle (ORC) for engine waste heat recovery. Energy 2011;36:3406–18.
[7] Wei D, Lu X, Lu Z, Gu J. Performance analysis and optimization of organic Rankine cycle (ORC) for waste heat recovery. Energy Convers Manage 2007;48:1113–9.
[8] Lecompte S, Aneel B, Ziviani D, van den Broek M, De Paepe M. Exergy analysis of zeotropic mixtures as working fluids in organic Rankine cycles. Energy Convers Manage 2014;85:727–39.
[9] Markides CN. Low-concentration solar-power systems based on organic Rankine cycles for distributed-scale applications: Overview and further developments. Front Energy Res 2015;3:67.
[10] Angelino G, Colonna Di Paliano P. Multicomponent working fluids for organic Rankine cycles (ORCs). Energy 1998;23(6):449–63.
[11] Wang JL, Zhao L, Wang XD. A comparative study of pure and zeotropic mixtures in low-temperature solar Rankine cycle. Appl Energy 2010;87 (11):3366–73.
[12] Garg P, Kumar P, Srinivasan K, Dutta P. Evaluation of isopentane, R-245fa and their mixtures as working fluids for organic Rankine cycles. Appl Therm Eng 2013;51(1–2):292–300.
[13] Chys M, Van Den Broeck M, Vanslambrouck B, De Paepe M. Potential of zeotropic mixtures as working fluids in organic Rankine cycles. Energy 2012;44(1):623–32.
[14] Heberle F, Preißinger M, Brüggemann D. Zeotropic mixtures as working fluids in organic Rankine cycles for low-enthalpy geothermal resources. Renew Energy 2012;37(1):364–70.
[15] Chen H, Goswami DY, Rahman MM, Stefanakos EK. A supercritical Rankine cycle using zeotropic mixtures as working fluids for the conversion of low-grade heat into power. Appl Therm Eng 2011;31(1):549–55.
[16] Sami SM. Energy and exergy analysis of an efficient organic Rankine cycle for low temperature power generation. Int J Ambient Energy 2008;29(1):17–26.
[17] Liu M, Shi Y, Fang F. A new operation strategy for CCHP systems with hybrid chillers. Appl Energy 2012;95:164–73.
[18] Li S, Wu JY. Theoretical research of a silica gel-water adsorption chiller in a micro combined cooling, heating and power (CCHP) system. Appl Energy 2009;86(6):958–67.
[19] Hajabdollahi H. Investigating the effects of load demands on selection of optimum CCHP-ORC plant. Appl Therm Eng 2015;87:547–58.
[20] Qiu G, Shao Y, Li J, Liu H, Riffat SB. Experimental investigation of a biomass-fired ORC-based micro-CHP for domestic applications. Fuel 2012;96:374–82.
[21] Khurana S, Banerjee R, Gaitonde U. Energy balance and cogeneration for a cement plant. Appl Therm Eng 2002;22(5):485–94.
[22] Nguyen TQ, Slawson JD, Boulama KG. Power generation from residual industrial heat. Energy Convers Manage 2010;51(11):2220–9.
[23] Karellas S, Leonartidis A-D, Panousis G, Bellos E, Kakaras E. Energetic and exergetic analysis of waste heat recovery systems in the cement industry. Energy 2013;58(1):147–56.
