

COMPUTER-AIDED WORKING FLUID DESIGN AND POWER SYSTEM OPTIMIZATION USING THE SAFT- γ MIE EQUATION OF STATE

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ABSTRACT

The achievement of economical designs of organic Rankine cycle (ORC) systems for deployment in a variety of applications can be greatly facilitated by computer-aided molecular design (CAMD) techniques, for which accurate and reliable group contribution (GC) equations of state (EoS) are required to predict the thermodynamic and transport properties of suitable working fluids. In this work, the capabilities of SAFT- γ Mie, a GC EoS, is extended to include functional groups such as $-\text{CF}_3$ and $>\text{CF}_2$, that can allow the design of environmentally-friendly refrigerant working fluids. The parameters of these groups in the SAFT- γ Mie EoS are regressed from experimental data. With these parameters, maximum average absolute deviations (AADs) from experimental data of 5 % for the vapour pressure, 3 % for the saturated liquid density and 3 % for the liquid-phase density are recorded, confirming the suitability of this EoS for working-fluid thermodynamic property predictions. Furthermore, by employing suitable GC methods, important transport properties such as the thermal conductivity, liquid viscosity and vapour viscosity are predicted with AADs of 28 %, 23 % and 6 %, respectively. The new GC parameters are implemented in an existing CAMD-ORC model and parametric optimization studies are completed. It is observed that for a 150 °C heat source, a refrigerant—heptafluorobutane—with net power output of 43 kW outperforms the best performing hydrocarbon working fluid (*n*-propane, 35 kW). This confirms the need to include refrigerants within the CAMD-ORC framework in addition to hydrocarbons. With heat sources at temperatures of 250 °C and 350 °C, the optimal working fluids are 2-pentene and 2-hexene corresponding to net power outputs of 137 kW and 219 kW, respectively.

KEY WORDS: equation of state, group contribution, optimization, ORC, SAFT- γ Mie, waste-heat recovery.

1. INTRODUCTION

Recently, sizable investments have been made in technologies that can utilize renewable energy sources and in technologies that can improve the efficiency of industrial processes and plants, in particular by the recovery of waste heat for power generation. Among the available technologies, organic Rankine cycle (ORC) systems have been identified as one of the attractive options for the recovery and conversion of low- and medium-grade waste heat into electricity [1]. Compared to the conventional water/steam Rankine cycle, the ORC—which makes use of a pure or mixtures of organic compounds as the working fluid—can in some cases offer higher thermal efficiencies for heat recovery in low temperature applications [1], including when converting geothermal heat [2], industrial waste heat [3–4], solar thermal heat [5], and thermal energy rejected from internal combustion engines, *e.g.*, from the exhaust gases [6].

Typically, the design of ORC systems requires the identification of a suitable working fluid, cycle architecture and operating conditions that can enable the most cost-effective utilization of the heat source. The large number of available working fluids and alternative cycle architectures (subcritical, transcritical, *etc.*) that need to be considered within the design space poses a highly challenging design and optimization problem. In conventional design methods [7–9], several fluids are screened based on prespecified performance criteria and

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heuristics, then the working fluid that emerges as optimal is used in parametric studies to determine the optimal cycle operating parameters. Although useful insights can be drawn for the performance of alternative fluids, these methods can lead to suboptimal systems since the influence of the working fluid on system performance is not considered. Furthermore, the approach focused on a preselected set of known working fluids; thus, they cannot be applied in studies where the aim is to identify a novel high-performing working fluid.

Unlike conventional methods, computer-aided molecular design (CAMD) methodologies [4, 10–13] integrate working fluid selection and system optimization into a unified framework, capturing explicitly the influence of the working fluid on system performance, allowing the design of novel working fluids, and eliminating the heuristics and subjective preselection of working fluids. Using CAMD methods, a fluid can be defined using a combination of molecular functional groups (*e.g.*, $-\text{CH}_3$, $>\text{CH}_2$, $>\text{CH}-$, $\text{CH}_2=$, $-\text{CH}=$, $-\text{CF}_3$, $>\text{CF}_2$), linked to satisfy bond constraints (*e.g.*, no free bonds). The key features of a typical CAMD formulation include a system model, a group contribution (GC) equation of state (EoS), molecular feasibility constraints, and an optimization algorithm. The model, here, describes the ORC system under consideration using mass and energy balances; the GC EoS utilizes the available molecular groups to determine fluid properties; the molecular feasibility constraints impose restrictions to avoid creating unrealistic fluids; and the optimization algorithm guides the search for optimal working fluid, system architecture and operating conditions.

The use of CAMD techniques to facilitate the design and optimization of ORC systems has gained significant attention in recent years. Previous studies have proposed a stepwise approach [14,15], in which a set of working fluids with desired properties are identified from CAMD, and later used for ORC system optimization. Subsequently, the approach was extended to working fluid mixtures [16]. More recently, a CAMD-ORC framework has been developed using an advance molecular GC EoS, SAFT- γ Mie [17], to facilitate simultaneous working fluid selection and cycle optimization from a thermodynamic viewpoint [3]. In later work, this framework was extended to include alternative cycle architectures [18] and system optimization based on techno-economic criteria [19]. However, the proposed CAMD-ORC frameworks typically support the design of hydrocarbon working fluids. Due to the large number of commercially available refrigerants with excellent thermodynamic properties and environmental performance criteria, it is of interest to extend the scope of these previous studies by allowing the investigation of refrigerant working fluids in terms of performance and cost, in addition to hydrocarbons. No previous studies have investigated refrigerant working fluids with CAMD approaches using the SAFT- γ Mie EoS.

In this paper, new group parameters for the functional groups $>\text{CF}_2$ and $-\text{CF}_3$ are presented, for use with the SAFT- γ Mie EoS, along with GC-method predictions for important critical and transport properties. This allows the simultaneous design of refrigerant working fluids and ORC systems for targeted applications. The remainder of this article is structured as follows. In Section 2, the methods applied to estimate the GC parameters of the functional groups $>\text{CF}_2$ and $-\text{CF}_3$ are presented. These are then used to predict thermodynamic (enthalpy, entropy, heat capacity) and transport (thermal conductivity, viscosity, surface tension) properties of relevant refrigerant fluids. In Section 3, the developed group parameters are implemented in a CAMD-ORC framework to facilitate the thermodynamic optimization of ORC systems in which the net power output is maximized. Finally, the conclusions from this work are summarized in Section 4.

2. PROPERTY PREDICTIONS

2.1 Thermodynamic properties: SAFT- γ Mie Equation of State

In the first instance, power-cycle heat engines including ORC systems, can be characterized by their thermodynamic performance. This necessitates the capability to predict the thermodynamic properties of the working fluid. While there are various EoS (including cubic equations) for this purpose, GC equations are better suited to the challenge of developing novel working fluids through CAMD techniques. To this end, the SAFT- γ Mie EoS (a group contribution version of the statistical associating fluid theory, SAFT, for variable range Mie

potentials) [17] is deployed. Within the SAFT- γ Mie EoS, the total Helmholtz free energy (A) of a molecule is described by a sum of four individual contributions:

$$\frac{A}{Nk_B T} = \frac{A^{\text{ideal}}}{Nk_B T} + \frac{A^{\text{mono.}}}{Nk_B T} + \frac{A^{\text{chain}}}{Nk_B T} + \frac{A^{\text{assoc.}}}{Nk_B T}, \quad (1)$$

where A^{ideal} is the free energy of the ideal gas, $A^{\text{mono.}}$ is a term accounting for interactions between monomeric Mie segments, A^{chain} is the contribution to the free energy for the formation of molecules from Mie segments, $A^{\text{assoc.}}$ is a term accounting for the association interactions, N is the total number of molecules, k_B is the Boltzmann constant, and T is the absolute temperature [17]. Thereafter, other key working fluid properties such as specific enthalpy, entropy, heat capacity, *etc.*, are calculated from A using standard thermodynamic relations.

In SAFT- γ Mie, each molecular group is defined by a set of parameters: the number ν_k^* of identical segments that the group comprises; the diameter σ_{kk} of the segments of the group; the energy of interaction ϵ_{kk} between the segments of the group; the values λ_{kk}^r and λ_{kk}^a of the repulsive and attractive exponents, respectively; and the shape factor S_k [17]. For the refrigerant-related molecular groups considered in this work, *i.e.*, $>\text{CF}_2$ and $-\text{CF}_3$, these parameters were developed in previous work and are presented in Table 1. With these parameters, the accuracy of the thermodynamic property prediction of perfluoroalkane molecules from SAFT- γ Mie EoS is assessed by comparing the theoretical property predictions to available experimental data.

Table 1 Group parameters for $>\text{CF}_2$ and $-\text{CF}_3$, estimated using experimental data obtained from NIST database, taken from Ref [20].

Functional group	ν_k^*	S_k [–]	σ_{kk} [Å]	(ϵ_{kk}/k_B) [K]	λ_{kk}^r [–]	λ_{kk}^a [–]
$>\text{CF}_2$	1	0.2752	5.198	459.92	33.963	6
$-\text{CF}_3$	1	0.5449	4.931	325.00	28.904	6

For the purposes of this comparison, five perfluoroalkane compounds suitable for use in ORC systems are considered, from perfluoroethane (C_2F_6) to perfluorohexane (C_6F_{14}). The corresponding percentage average absolute deviation AAD (%) of the theoretical calculations from the experimental data for the investigated properties of these working fluids are presented in Table 2. The working-fluid properties investigated are the saturation vapour pressure (P_{sat}) and saturated liquid density (ρ_{sat}), and the liquid-phase density (ρ_{liq}). Although other properties are also of interest in performing thermodynamic cycle analyses of ORCs, these parameters are considered to provide a representative indication of the suitability of the SAFT- γ Mie EoS.

Table 2 Average absolute deviation, AAD (%), for the vapour pressure P_{sat} , saturated liquid density ρ_{sat} , and liquid-phase density ρ_{liq} of selected perfluorocarbons obtained with the SAFT- γ Mie EoS relative to experimental data from NIST, n denotes the number of experimental data points used in the calculation.

Compound	T range [K]	n	AAD [%] P_{sat}	T range [K]	n	AAD [%] ρ_{sat}	T range [K]	P range [bar]	n	AAD [%] ρ_{liq}
C_2F_6	173–283	12	5.07	173–283	12	2.90	200–280	10–300	147	3.44
C_3F_8	126–341	44	3.31	126–341	44	1.76	200–340	1–200	159	1.41
C_4F_{10}	189–379	39	3.30	189–379	39	1.46	200–386	1–300	329	1.65
C_5F_{12}	200–420	45	4.42	200–420	45	1.39	200–421	1–300	391	1.27
C_6F_{14}	200–440	49	3.23	200–440	49	0.89	283–313	1–300	93	0.19

The comparison between these saturated properties are also presented in Fig. 1, where it is seen that the SAFT- γ Mie EoS presents a good description of these properties. For ORC systems where a substantial amount of energy is expended on evaporating the working-fluid, it is important to examine the phase-change enthalpies calculated from SAFT- γ Mie. The phase-change enthalpies calculated from SAFT- γ Mie are compared with those available from experiments as shown in Fig. 1c, where the EoS is also seen to provide good descriptions of the enthalpy of vaporization of the five perfluoroalkane. In addition, the specific heat capacities of perfluoropentane as functions

of temperature are presented in Fig. 1d, where the isobars have been chosen to span both subcritical and supercritical regions and both condensed-liquid and superheated-vapour regions. This is done to show the suitability of deploying SAFT- γ Mie in predicting another important property with respect to ORC systems. With the exception of the slight deviations observed close to the critical region (for the 15-bar isobar), the descriptions provided here are also in good agreement with expectations from experiments. The capability of SAFT- γ Mie to predict with accuracy relevant thermodynamic properties that were not used in the model-parameter development, *i.e.*, the enthalpies of vaporization and the specific heat capacities, as well as the saturated-vapour densities, demonstrates its suitability for use in CAMD of working fluids for ORC systems.

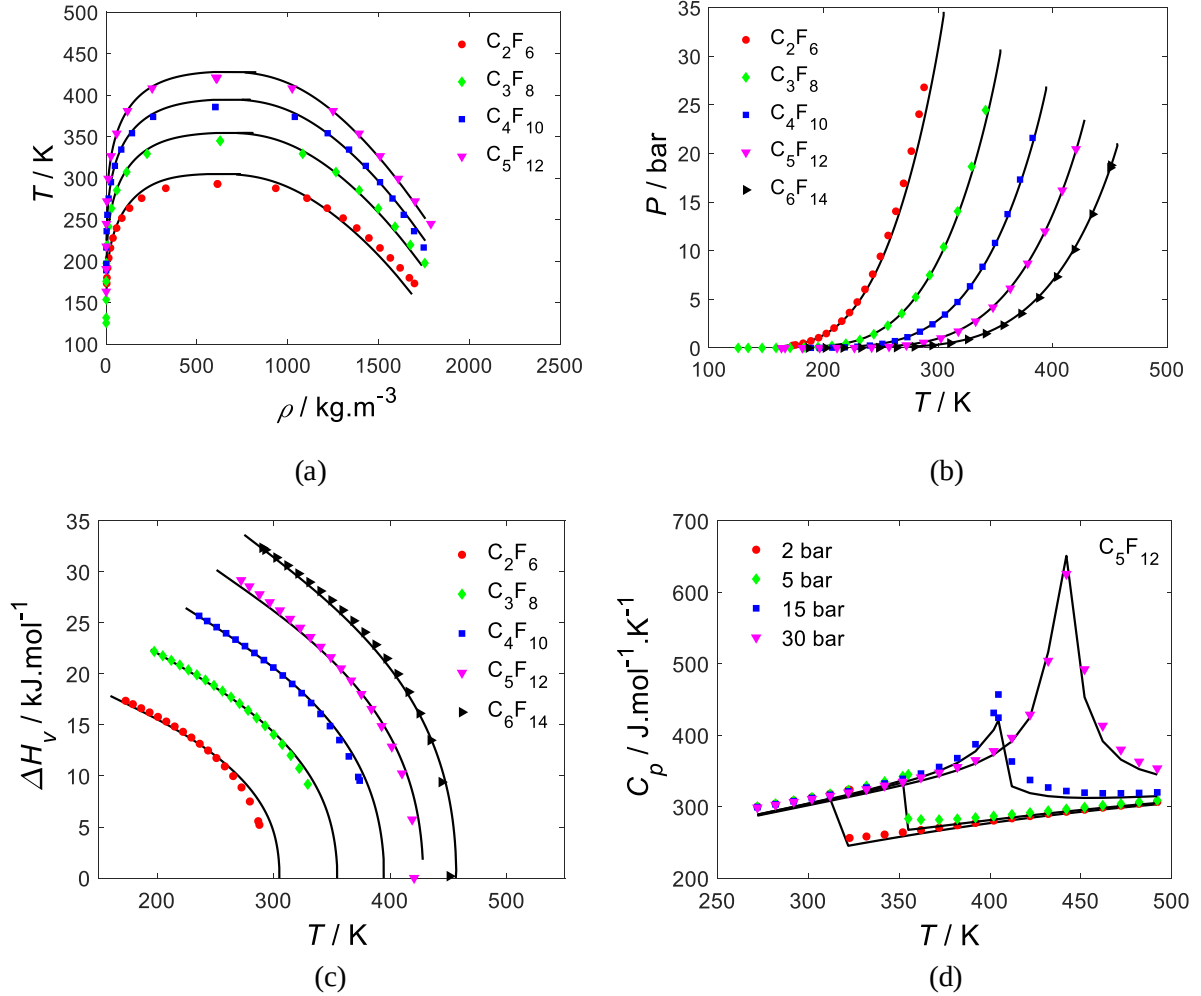


Fig. 1 Thermodynamic properties of selected perfluorocarbons: (a) temperature-density coexistence curve; (b) vapour pressure curve; (c) latent heat of vaporization; and (d) temperature dependent isobaric heat capacity, C_p . Comparison of experimental data obtained from NIST REFPROP (symbols) and predictions from the SAFT- γ Mie equation of state (continuous curve).

2.2 Critical and transport properties

In Section 2.1, the SAFT- γ Mie EoS was shown to predict accurately selected thermodynamic properties of perfluorocarbons. However, this does not allow the prediction of critical and transport properties of fluids. These properties—such as the critical temperature, pressure and volume, thermal conductivity, dynamic viscosity, and surface tension—are essential when performing thermo-economic calculations and when estimating, for example, heat transfer coefficients that are required in the sizing of heat transfer units.

In previous work [3], GC methods [21–25] for estimating the critical and transport properties relevant to ORC systems have been presented and discussed. Functional groups such as $-\text{CH}_3$, $>\text{CH}_2$, $>\text{C}<$, $>\text{CH}-$, $\text{CH}_2=$ and $>\text{CH}=$ were employed to predict relevant properties (T_c , P_c , V_c , η_L , η_V , λ_L , λ_V and σ) of hydrocarbon working fluids. The authors concluded that these methods are adequate for the prediction of these desired properties.

However, the GC methods did not include group parameters for $>\text{CF}_2$ and $-\text{CF}_3$, which are essential in calculating the properties of key refrigerants (*e.g.*, trifluoropropane, R-263). In this section, the capability of the GC methods is extended to allow the prediction of critical and transport properties of refrigerants.

2.2.1 Parameter estimation. A key step in the estimation of GC parameters is the collection of reliable experimental data for compounds comprising the relevant groups. In this work, data for all properties of interest were collected from the NIST REFPROP database [26], and divided into ‘training’ and ‘testing’ subsets. The former set is used for parameter estimation, whilst the latter is used to assess the predictive quality of the GC methods and the estimated group parameters. Both training and testing set consist of the same nine compounds, from C_2F_6 to $\text{C}_{10}\text{F}_{22}$, covering small to large molecular weight compounds. Although this work considers only straight chain perfluorocarbons, compounds including $>\text{CF}_2$ and $-\text{CF}_3$ groups with other functional groups (*e.g.*, $\text{C}_2\text{H}_3\text{F}_3\text{O}$) can also be used, provided reliable experimental data for those compounds are available.

By considering the relevant GC equations (see Section 2.2.2), the data in the training set is employed to estimate the group parameters of functional groups $>\text{CF}_2$ and $-\text{CF}_3$ using standard regression techniques. The objective function selected for the regression can have an impact on the regressed parameters. Various forms of objective function such as the mean square error, maximum absolute deviation, average absolute percent deviation, *etc.*, can be used; without loss of generality, the sum absolute deviation (AD) is used in this work, as it has been shown to provide a good estimation of the deviations between predictions and data [21]:

$$\min \text{AD} = \sum_{n=1}^n |P_i^{\text{exp}}(T_i) - P_i^{\text{calc}}(T_i)|, \quad (2)$$

where AD is the sum of absolute deviation between model prediction and experimental data; P is the property of interest (*e.g.*, ideal gas heat capacity, C_p^0); T accounts for the dependency of a property on temperature; n is the total number of samples; superscripts ‘exp’ and ‘calc’ denote experimental and calculated properties respectively. To this end, a derivative free optimization algorithm [27] is applied to adjust the model parameters until the error between the model prediction and experimental data is minimized. Section 2.2.2 presents the GC relations based on which Eq. 2 is employed.

2.2.2 Relations used in parameter estimation. The GC methods used in the parameter estimation can be found in Ref. [3]. Nevertheless, for the sake of completeness, the relevant relations are summarized below.

Ideal gas heat capacity: This property for perfluorocarbons is predicted using the Joback and Reid GC approach [21], which correlates heat capacity as a function of temperature, with four adjustable parameters:

$$C_p^0 = \sum a_i - 37.93 + [\sum_i b_i + 0.210]T + [\sum_i c_i - 3.91 \times 10^{-4}]T^2 + [\sum_i d_i + 2.06 \times 10^{-7}]T^3, \quad (3)$$

where C_p^0 is the ideal gas heat capacity in J/mole K; T is temperature in K; and a , b , c , and d are the adjustable group parameters of the model.

Critical pressure, temperature and volume: Here, the Joback and Reid GC methods [21] are used to predict critical pressure, temperature, and volume:

$$P_c = (0.113 + 0.0032n_A - \sum_i P_{c,i})^{-2}; \quad (4)$$

$$T_c = T_b \left[0.584 + 0.965 \sum_i T_{c,i} - (\sum_i T_{c,i})^2 \right]^{-1}; \quad (5)$$

$$V_c = 17.5 + 0.965 \sum_i V_{c,i}; \quad (6)$$

where P_c (in bar), T_c (in K), and V_c (in cm^3/mole) are the critical pressure, temperature and volume; n_A is the total number of atoms; T_b is the normal boiling temperature; and $P_{c,i}$, $T_{c,i}$, and $V_{c,i}$ are adjustable group parameters.

Dynamic viscosity: The liquid-phase dynamic viscosity for straight chain compounds is estimated using the Joback and Reid correlation [21]:

$$\eta_L = M \exp \left[\frac{(\sum_i \eta_{a,i} - 597.82)}{T} + \sum_i \eta_{b,i} - 11.202 \right], \quad (7)$$

where η_L , in units of Pa.s, denotes the liquid viscosity; T is temperature in K; M is the molecular weight of the given molecule; $\eta_{a,i}$ and $\eta_{b,i}$ are the adjustable group contribution parameters. For branched compounds, the correlation of Sastri and Rao [28] can be used instead, as the Joback and Reid correlation has been shown to produced large errors in this case [3]. (Note that only the parameters of Joback and Reid method are estimated in this work, as that of Sastri and Rao's method are available in Ref. [28].)

For the estimation of vapour phase dynamic viscosity, the method of Reichenberg [29] is used, which accounts for temperature, molecular weight, and dipole moment of compounds:

$$\eta_V = \frac{M^{1/2} T}{\sum_i n_i C_i [1 + (4/T_{cr})][1 + 0.36 T_r (T_r - 1)]^{1/6}} \times \frac{T_r (1 + 270 \mu_r^4)}{T_r + 270 \mu_r^4}, \quad (8)$$

where η_V is the vapour phase dynamic viscosity in units of microPoise; T_{cr} and T_r are critical and reduced temperature respectively; μ_r denotes the reduced dipole moment; n_i is the number of groups in a molecule; C_i is the adjustable group parameter, which is determined in this work. Note that Eq. 8 is applicable at low pressure, for high pressure fluids, Reichenberg suggested a correction factor which can be found in Ref. [29].

Thermal conductivity: The liquid- and vapour-phase thermal conductivities are estimated using the methods proposed by Sastri and Rao [22] and Chung *et al.*, [30], respectively:

$$\lambda_L = \sum_i \lambda_{b,i} \times a^m \quad (9); \quad m = 1 - \left(\frac{1 - T_r}{1 - T_{b,r}} \right)^n. \quad (10)$$

In Eqs. 9 and 10, $\lambda_{b,i}$ denotes the GC at normal boiling point; $a = 0.856$ and $n = 1.23$ for alcohols and phenols; and $a = 0.16$ and $n = 0.2$ for other compounds. The liquid thermal conductivity in W/(m.K) is calculated from:

$$\frac{\lambda_V M'}{\eta_V C_V} = \frac{3.75 \Psi}{C_V / R}. \quad (11)$$

In Eq. 11, M' (in kg/mol) and R (in J/(mol.K)) are molar mass and ideal gas constant; C_V (in J/(mol.K)) and η_V (in N.s/m²) are the specific heat capacity at constant volume and low-pressure vapour phase viscosity; and Ψ is calculated as using the correlation presented in Ref. [30].

Surface tension: The method of Sastri and Rao [24] is used here to predict the surface tension at the normal boiling point and then extends this to other, specified temperatures. The input parameters include critical temperature and pressure, and normal boiling temperature. The critical properties can be calculated using the Joback and Reid method, whilst the normal boiling point is estimated using SAFT- γ Mie EoS:

$$\sigma = K P_{cr}^x T_b^y T_{cr}^z \left[\frac{1 - T_r}{1 - T_{b,r}} \right]^m, \quad (12)$$

where σ (in mN/m) denotes the surface tension, K , x , y , z and m are given as 0.158, 0.50, -1.5, 1.85 and 11/9, respectively, for compounds other than alcohols and phenols, P in bar, and T in Kelvin.

2.2.3 Estimated group parameters. The parameters of $>CF_2$ and $-CF_3$ for critical and transport properties are estimated via the approach presented in Section 2.2.1, and are reported in Tables 3 and 4. Before implementing the parameters, it is necessary to check their validity across broad temperature and pressure ranges relevant to

ORC system operation. To this end, the testing set data are employed to calculate the AAD for all properties, except the critical ones for which relative errors were calculated. These are reported in Tables 5 and 6.

Table 3 Estimated group contributions for $>\text{CF}_2$ and $-\text{CF}_3$, obtained by minimizing the absolute difference between the model predictions (Eqs. 3 to 6) and experimental data from NIST.

Functional group	$T_{c,i}$	$P_{c,i}$	$V_{c,i}$	Ideal gas heat capacity constants			
				a	b	c	d
$>\text{CF}_2$	0.02248	-0.0026	83.4138	-1.06×10^1	2.54×10^{-1}	-3.01×10^{-4}	1.10×10^{-7}
$-\text{CF}_3$	0.04907	-0.02191	103.760	1.60×10^1	1.55×10^{-1}	-8.16×10^{-5}	-6.43×10^{-9}

Table 4 Estimated group contributions for $>\text{CF}_2$ and $-\text{CF}_3$, obtained by minimizing the absolute difference between the model predictions (Eqs. 7, 8, and 9) and experimental data from NIST.

Functional group	$\eta_{v,i}$	$\lambda_{L,i}$	η_L	
			$\eta_{a,i}$	$\eta_{b,i}$
$>\text{CF}_2$	6.31	-0.00682	209.42	-0.4155
$-\text{CF}_3$	12.89	0.0384	586.74	-2.5170

Table 5 Percent deviation determined for perfluorocarbons included in the parameter estimation. The data employed in the validation of the ideal gas heat capacity consists of 22 points, in the range of 200 K to 653 K.

Compound	T_c , % RE	P_c , % RE	V_c , % RE	C_p^0 , % AAD
C_2F_6	0.5	1.4	0.0	1.3
C_3F_8	0.1	0.0	2.9	1.6
C_4F_{10}	0.0	0.6	1.3	1.9
C_5F_{12}	0.5	1.9	0.6	2.1
C_6F_{14}	0.3	0.1	0.7	2.2
C_7F_{16}	0.3	3.9	0.6	2.3
C_8F_{18}	0.0	8.5	0.7	2.3
C_9F_{20}	2.8	11.9	1.1	2.4
$\text{C}_{10}\text{F}_{22}$	2.9	13.7	0.0	2.4

Table 6 Average absolute deviation, AAD (%), for the liquid phase viscosity η_L , vapour phase viscosity η_v , and liquid phase thermal conductivity λ_L of selected perfluorocarbons obtained with the GC methods (Eqs. 7, 8, and 9) relative to experimental data from NIST, n denotes the number of data point used in the calculation.

Compound	η_L			η_v			λ_L		
	T range [K]	n	% AAD	T range [K]	n	% AAD	T range [K]	n	% AAD
C_2F_6	273–286	42	6.5	273–425	42	1.7	273–278	42	3.6
C_3F_8	273–311	42	11.1	273–440	42	1.6	273–311	42	17.4
C_4F_{10}	273–348	42	23.7	280–500	42	4.4	273–347	42	26.0
C_5F_{12}	273–378	42	8.0	320–500	42	3.9	273–378	42	3.6
C_6F_{14}	273–406	42	5.1	340–670	42	2.7	273–400	42	13.4
C_7F_{16}	298–429	42	5.6	360–673	42	6.7	273–420	42	10.6
C_8F_{18}	298–452	42	5.8	380–673	42	1.8	273–450	42	28.4
C_9F_{20}	298–472	42	6.6	390–673	42	1.7	273–470	42	0.9
$\text{C}_{10}\text{F}_{22}$	298–488	42	2.2	410–673	42	1.5	273–480	42	13.8

The estimated critical properties (shown in Table 5) for all the selected perfluorocarbons are in good agreement with their corresponding experimental values, with percent relative error range of 0.00 to 2.97, 0.00 to 13.7, and 0.00 to 2.9 for T_c , P_c , and V_c , respectively. Unlike the critical properties, the parameters for the ideal gas heat capacity were tested over a given temperature range, 200 K to 653 K. The estimated results show reasonable agreement with experimental data. In this work, the ideal gas heat capacity, C_p^0 , is used to calculate the ideal gas Helmholtz free energy term, A^{ideal} in the SAFT- γ Mie EoS (see Eq. 1). This is achieved by first integrating $C_p^0(T)$ to obtain enthalpy, H^{ideal} , and then C_p^0/T to obtain entropy, S^{ideal} .

Although the Joback and Reid correlation employed to estimate the liquid-phase viscosity consists of only two group parameters that are independent of pressure, the validation results presented in Table 6 show reasonable agreement with experimental data, with a largest deviation of 23 % observed for perfluorobutane. This deviation is of similar magnitude to the maximum deviation reported in the original work by Joback and Reid [21]. Similarly, the single-phase vapour viscosity estimated using Reichenberg's method is compared against data from NIST REFPROP a function of temperature and pressure. Here, the pressure is fixed at 1 bar, whilst the temperature ranges from 273 K to 673 K. This range corresponds to a typical working temperature of ORC systems. From the validation results reported in Table 6, there is no significant deviation between the model predictions and their corresponding experimental values. This observation could be attributed to the ability of the model to capture the effect of dipole moment of the polar perfluorocarbon compounds.

A similar validation is performed for liquid-phase thermal conductivity. As in the original work by Sastri and Rao [22], saturated liquid thermal conductivity data is used. The maximum temperature in the testing set is limited to 90 % of the experimental critical value, which is a reasonable assumption since the group contribution will be applied to study a subcritical ORC system. The percent deviation ranges from 0.9 % to 28 %. For most of the perfluorocarbons, the predictions are relatively good away from the critical temperature, and gradually deteriorate as the critical temperature is approached. A similar trend is reported in Ref. [22].

Overall, the validation results demonstrate the adequacy of the group contribution methods in estimating the properties of perfluorocarbon compounds, using the newly developed $>\text{CF}_2$ and $-\text{CF}_3$ group parameters. Although large deviations were observed for a few cases, the deviations compare favourably well with literature values, and are considered reasonable for engineering calculations.

3. CASE STUDY: OPTIMIZATION OF ORC SYSTEMS

The CAMD-ORC model adopted in this work has been used previously in Ref. [3] to design subcritical ORC systems with hydrocarbon (HC) working fluids. The purpose of the present case study is to extend the existing CAMD-ORC model to account for the design of refrigerant working fluids, beyond hydrocarbons. This is achieved by incorporating the group parameters of $>\text{CF}_2$ and $-\text{CF}_3$ (developed in this work) into the existing model, allowing the calculation of properties of refrigerant fluids. In the next step, the CAMD-ORC model is used in a parametric optimization study to investigate the effects of refrigerant and hydrocarbon working fluids on system performance for different heat-source conditions: 150 °C, 250 °C, and 350 °C. In each case, the heat capacity flow rate of the heat source and sink are 4.2 kW/K and 21 kW/K, respectively, with a fixed heat sink temperature of 15 °C. The simulations are completed by specifying pump and expander efficiencies, for which values of 0.7 and 0.8 are used, respectively, in addition to a minimum approach temperature in the condenser, of 5 °C.

The working-fluid families considered in this study are presented in Table 7. For a given working-fluid family and heat source temperature, the $>\text{CH}_2$ or $>\text{CF}_2$ group is varied and the cycle operating parameters (condensation temperature, reduced pressure, degree of superheat and minimum approach temperature) are optimized. The results obtained from this study are reported in Fig. 2.

Table 7 Molecular groups considered for the working fluid design.

Working fluid family	General molecular structure
<i>n</i> -alkanes (HC)	$\text{CH}_3-(\text{CH}_2)_n-\text{CH}_3$
iso-alkanes (HC)	$(\text{CH}_3)_2-\text{CH}-(\text{CH}_2)_n-\text{CH}_3$
1-alkenes (HC)	$\text{CH}_2=\text{CH}-(\text{CH}_2)_n-\text{CH}_3$
2-alkenes (HC)	$\text{CH}_3-\text{CH}=\text{CH}-(\text{CH}_2)_n-\text{CH}_3$
hydrofluorocarbon (HFC)	$\text{CH}_3-(\text{CF}_2)_n-\text{CF}_3$
hydrofluoroolefin (HFO)	$\text{CH}_2=\text{CH}-(\text{CF}_2)_n-\text{CF}_3$

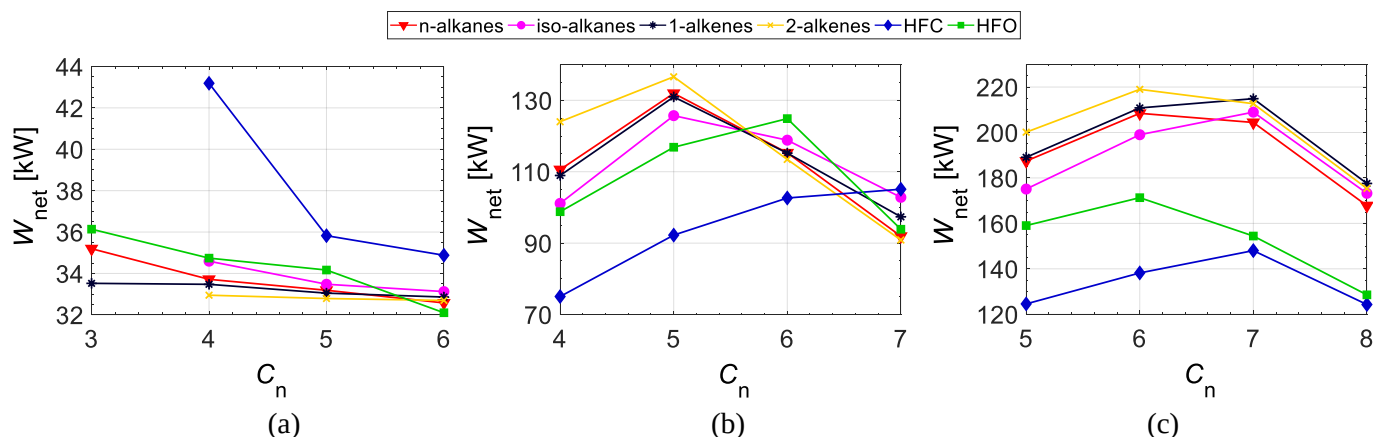


Fig. 2 Net power output obtained from an optimal ORC, which uses pure hydrocarbon (*n*-alkanes, iso-alkanes, 1-alkenes and 2-alkenes) and refrigerant (hydrofluorocarbon and hydrofluoroolefins) working fluids: (a), (b) and (c) represent results for cycle operated at heat source temperature of 150 °C, 250 °C and 350 °C respectively, and C_n is the number of carbon atom in the working fluid.

In Fig. 2, the well-performing working fluids based on net power output, identified for the 150 °C, 250 °C, and 350 °C heat sources are heptafluorobutane, 2-pentene and 2-hexene, respectively, with corresponding maximum power outputs in these three cases: 43 kW, 137 kW, and 219 kW. As expected, the power output increases as the heat-source temperature is increased. For the 150 °C heat source, the refrigerant working fluids (HFC and HFO) outperform the hydrocarbon fluids, with the best performing refrigerant (heptafluorobutane) showing a 19 % increase in power output compared with the best performing hydrocarbon fluid (*n*-propane). This observation indicates the benefit of extending the CAMD-ORC model to include the design of refrigerant working fluids, in addition to hydrocarbons. Furthermore, when the heat source temperature is increased, hydrocarbons of increased molecular size perform well, whilst for the refrigerants, beyond 150 °C, the optimal working fluid size does not change (i.e., C_7 and C_6 for HFC and HFO, respectively). Apart from the refrigerants, the trend observed for hydrocarbons have been reported in Ref. [3]. In addition, HFOs show a different trend compared to hydrocarbon working fluids between C_5 and C_6 . This results from the fact that hydrocarbon working fluids exhibit a large latent heat of vaporisation, h_{lv} , thus the evaporation pressure is limited by the pinch conditions, leading to less heat extraction and power generation. On the other hand, the HFOs have relatively small h_{lv} , allowing high evaporation pressure to be reached without being constrained by the pinch conditions.

For each working-fluid family, there appears to be an optimal working fluid, which is not necessarily the overall optimal for the given heat source. This observation justifies the ability of the optimization method of finding optimal working fluids across chemical families and applications.

4. CONCLUSIONS

In this paper, new molecular groups were integrated into a CAMD-ORC optimization framework, that make this suitable for the simultaneous, integrated design of the working fluid and of the overall ORC power system. This was motivated by the aim to develop optimal refrigerant working fluids that contain the $>CF_2$ and $-CF_3$ molecular groups, for ORC systems from a CAMD approach specifically based on an advanced GC EoS, namely SAFT- γ Mie, in which the thermodynamic properties of working fluids are predicted with the SAFT- γ Mie EoS. Following the implementation of SAFT- γ Mie group parameters for $>CF_2$ and $-CF_3$ obtained from literature, the EoS was shown to give accurate predictions of selected thermodynamic properties of interest, i.e., enthalpy of vaporization, specific heat capacity, and liquid- and vapour-phase densities of a range of perfluoroalkane working fluids, demonstrating its suitability for used in the wider CAMD-ORC framework. In addition, GC parameters for the molecular groups $>CF_2$ and $-CF_3$ were developed in this work, to enable the

accurate prediction of the necessary transport properties of the refrigerant working fluids. In a case study of ORC systems in waste-heat recovery applications spanning a range of temperatures from 150 °C to 350 °C, the hydrocarbon working fluids (2-alkenes in particular) appeared to be optimal at the higher end of heat-source temperatures (> 250 °C), while interestingly, the refrigerant working fluids outperformed the hydrocarbons by up to 19 % at the lower heat-source temperature of 150 °C.

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