

Article

An Effective Method for Working Fluid Design of Organic Rankine Cycle

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Abstract: This paper addresses an effective method for the selection and design of optimal working fluids of organic Rankine cycle (ORC) based on quantitative working fluid selection rules, aiming to reduce the complexity and improve the calculation efficiency of the working fluid design model. In the proposed method, the critical properties of the optimal working fluids for the given heat sources are first explored and summarized based on the quantitative relationship obtained by existing research and simulations. Based on the concept of working fluid substitution, the critical properties of the optimal pure working fluid are then adopted to target the optimal mixture working fluid by solving a modified computer-aided molecular-mixture design (CAMD) model and the ratio r of critical pressure to critical temperature is also strictly constrained to ensure a better working fluid. The component and the composition of the mixture working fluid are, thus, determined simultaneously. Results showed that both the designed pure and mixture working fluids have better performance than the existing ones determined by the selection and design rules. The targeted mixture working fluid enables one to achieve at least similar systematic efficiency and a better exergy efficiency in ORC than pure working fluid featuring similar critical properties. The application of the proposed method and model is finally verified via a practical case study.



Citation: Tang, J.; Kang, L.; Liu, Y. An Effective Method for Working Fluid Design of Organic Rankine Cycle. *Processes* **2022**, *10*, 1857. <https://doi.org/10.3390/pr10091857>

Academic Editor: Alfredo Iranzo

Received: 13 August 2022

Accepted: 6 September 2022

Published: 15 September 2022

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Keywords: organic Rankine cycle; working fluid design; process simulation; system optimization

1. Introduction

Organic Rankine cycle (ORC) is one of the most promising techniques for the recovery of low-temperature waste heat, whose performance strongly depends on the selection of working fluid [1]. In general, the working fluid with stable chemical properties, high safety, low greenhouse effect and ozone breaking capacity, abundant reserves and low cost are usually preferred [2]. However, when taking all those factors and the actual application scenarios into consideration, the number of commonly available working fluids (<20) will be far fewer than that of the existing ones (>300) [3]. It suggests that the existing working fluids or their mixtures may not meet the requirement of waste heat recovery in actual industries as perfect as possible.

The computer-aided molecular-mixture design (CAMD) technique can design completely new molecules or mixtures according to the actual requirements from functional groups [4], which offers the new possibility to handle the problem of working fluid design for ORCs [5]. Papadopoulos et al. [6] first proposed the systematic design and selection of the optimal working fluids method for ORCs based on CAMD and process optimization techniques. Fifteen molecular and process-related properties were generalized to provide guidelines for working fluid selection and design. The method can effectively select and design the working fluid to maximize the thermodynamic performance and economy of the ORC system while emphasizing the safety and environmental impacts. Based on this, Palma-Flores et al. [7] established a mixed mixed-integer nonlinear programming

(MINLP) model with four independent key properties of designed working fluids as objective functions to realize optimal waste heat recovery. The performance of three different ORC configurations was also analyzed. The result showed that the designed new organic compounds can effectively increase energy recovery and reduce toxicity in comparison to the existing working fluids. Palma-Flores et al. [8] also improved their method and model to realize simultaneous working fluid design and ORC configuration optimization for further increasing the thermodynamic efficiency of low-temperature waste heat recovery. To reduce the model complexity, the number of coupled cycles was fixed to three and the configuration optimization was achieved by enumeration. It was found that the thermodynamic performance of the coupled system increased by 9.8% when compared with the single system. The new designed working fluid showed 5.7% improvement for thermodynamic performance with respect to the commonly used working fluids. In addition, the safety index of the designed working fluid also improved significantly. Lampe et al. [9] used PC-SAFT (perturbed chain statistical associating fluid theory) equation of state to the ORC system optimization and a two-step solution strategy was adopted. In the first continuous-molecular targeting (CoMT) step, the hypothetical optimal working fluid and process parameters were determined. The new working fluid was then designed to close to the hypothetical target in the second step. It suggests that the proposed framework can effectively identify the optimal working fluid ranking list for the goal of maximizing the net output with relatively high accuracy. Based on this, Schilling et al. [10] proposed a one-stage CoMT-CAMD approach to achieve working fluids and process optimization for ORC. Since the PC-SAFT combined group contribution method (GCM) [11] was adopted to calculate the thermodynamic and transport properties, the established MINLP model can efficiently be solved using a deterministic algorithm and PC-SAFT can provide the feasibility to integrate a more detailed ORC model into the optimization framework [12]. This method is capable of effectively screening the best fluids in existing databases and newly designing the most promising molecular structures. Schilling et al. [13] integrated the detailed equipment model (i.e., heat exchanger and turbine, etc.) into a one-stage CoMT-CAMD framework with the system economy and thermodynamic performance as objective functions to explore the optimal design of mixture working fluids. The multi-scale integrated model was then solved in commercial software GAMS with external functions [14]. The result showed that the pure working fluids have more thermos-economic benefits while the mixture working fluids can increase the net power output by 5.7% when compared with pure ones. Kleef et al. [15] established a multi-objective MINLP optimization framework with the consideration of thermodynamic economic performance for ORC working fluid design and process optimization. In this work, the equation of state SAFT- γ Mie was adopted to determine thermodynamic properties and GCM was used to predict critical and transport properties. Further, NSGA-II was employed to solve the multi-objective MINLP model. It implies that there is a trade-off between specific investment cost and net power output and the proposed framework can simultaneously achieve the optimal design of ORC systems and working fluids for variable heat-source temperatures and capacities. Luo et al. [16] introduced an artificial neural network (ANN)-based property prediction model to the working fluids design and ORC process optimization framework to improve the prediction accuracy of properties. A step-wise strategy was then developed to improve calculation efficiency. Results showed that the absolute average deviation (AAD) of working properties calculated by the proposed approach can be greatly reduced. The AAD of thermal efficiency for existing working fluids can reduce by 26–81% and the calculation time can reduce by several orders of magnitude compared with previous methods.

In the typical CAMD-based method for the design of ORC working fluids, the problem is usually formulated as a complex MINLP model that involves the process and thermodynamic state model, properties prediction model and a constitutive model [14]. Among these models, the GCM-based properties prediction model and the constitutive model are relatively simple and easy to solve, whereas the process and thermodynamic state model is strongly nonlinear [17], especially when the actual vapor–liquid equilibrium calculation terms for evaporating and condensing are introduced in the design scenario of mixture working fluids [18]. Hence, the typical CAMD-based model for the design of mixture working fluid can hardly be solved directly in an acceptable time. To the best of our knowledge, such a model can only be solved under certain conditions [18] or using complex solving strategies [19] and in almost all studies, the component and composite of the mixture working fluid are determined in a stepwise manner. Although such practices are effective and useful, the calculation process is somehow tedious, resulting in the final solution being only a feasible solution or a local optimal solution, which may further limit the application of the CAMD technique in the design of ORC working fluids. Among the few methods of simultaneous design [10,14], the complex thermodynamic theory and equation of state are contained, which is unhelpful to engineers in practical engineering applications.

To address these problems, this work aims to develop an effective method for working fluid design with the consideration of the quantitative criteria for working fluid selection. In this method, the influences of the critical properties of working fluids on the ORC performances are first explored and generalized to construct a quantitative relationship between the properties of waste heat sources and working fluids via simulation. By replacing the process and thermodynamic state model with the quantitative relationship, the optimal mixture working fluid, including its component and composite, is simultaneously determined by solving a simplified CAMD model. In this way, the complex nonlinear process and thermodynamic state model is omitted and the feasibility and solving efficiency of the CAMD model can be significantly improved. Furthermore, the proposed method is simple and intuitive and is more conducive to providing guidance for practical industrial design.

2. Design of Mixture Working Fluid for ORC

Mixture working fluids are composed of two or more pure working fluids mixed in a certain proportion. Unlike the pure working fluids, mixture working fluid undergoes non-isothermal phase change during the evaporation [20]; the temperature increase in the phase change during evaporating process will cause a better heat transfer matching between the working fluid and the waste heat stream. The irreversible loss in the heat recovery process can, thus, be reduced and the system performance can, thus, be maintained [21]. It has been pointed out that the selection rules for pure working fluids are still reliable for mixture working fluid selection [22]. Therefore, it is natural that if we can find a mixture working fluid that has similar critical properties to the optimal pure working fluid of the given heat source, the mixture working fluid can be considered as a better choice for the ORC.

Figure 1 shows the detailed methodology for the design of mixture working fluid for ORCs. As shown in Figure 1, based on the ORC process simulation and polynomial fitting, the quantitative rules for the selection of pure working fluid are generalized. These quantitative rules are then used to target the optimal design of mixture working fluid by solving a simplified CAMD model so that the component and composite of the mixture working fluid are determined at the same time. Note that the CAMD method can not only design the optimal mixture working fluid that is composed of two or more existing pure working fluids but also design the completely new working fluids according to the actual applications.

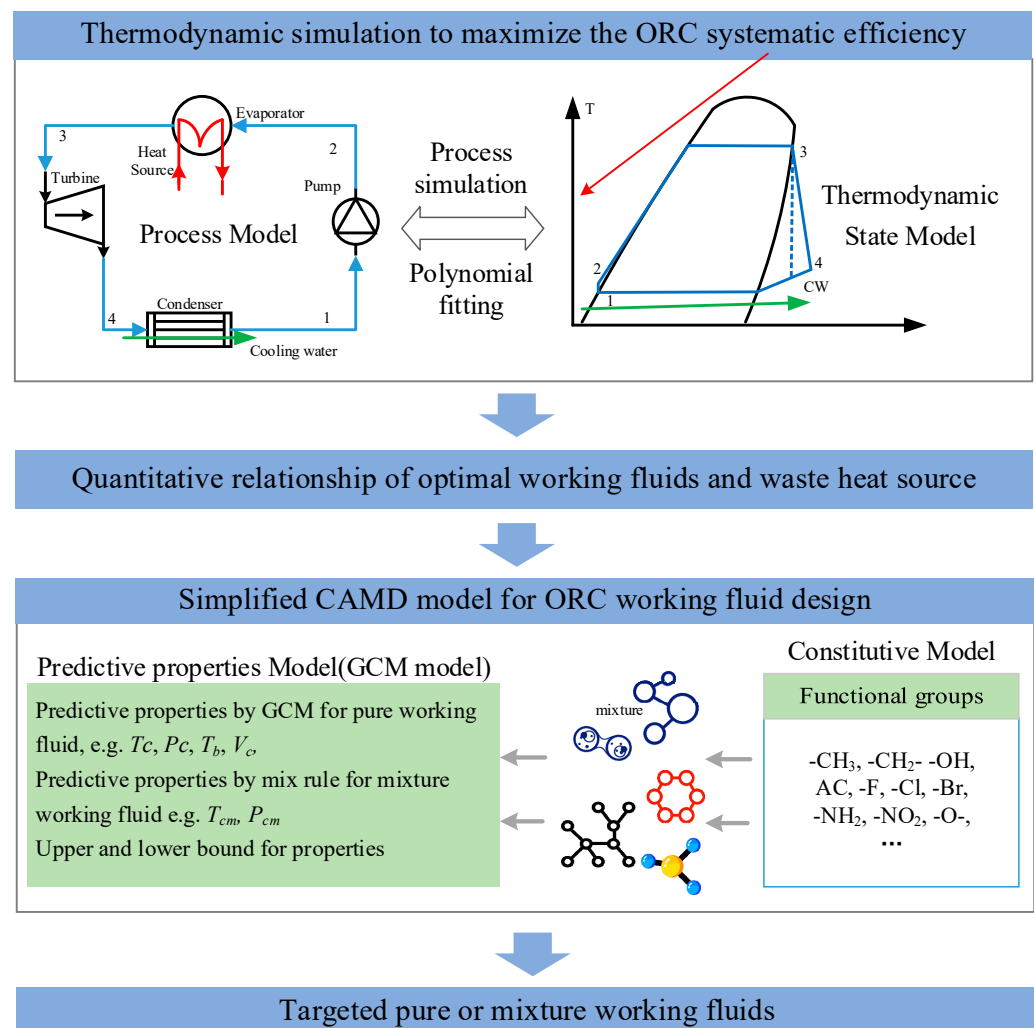


Figure 1. The methodology for the design of working fluids.

2.1. Quantitative Rules for the Selection of Pure Working Fluid

In the past few years, extensive research activities have been focused on the criterion for the selection of the pure working fluid of ORC and a series of qualitative and quantitative principles have been proposed. It has been pointed out that the heat source temperature and the critical temperature of pure working fluid are the two most important criteria for the selection of working fluid [23]. When the difference between the inlet temperature of waste heat and the critical temperature of pure working fluid is in a range of 35 K to 55 K, the heat recovery performance of the system will be better [24]. In particular, for a basic ORC system, the optimal pure working fluid can be achieved when the temperature difference reaches about 40 K [25] and a linear relation between the inlet temperature of waste heat and the critical temperature of its optimal pure working fluid is proposed, so that the optimal pure working fluid for a given waste heat can be easily determined [26]. However, this relationship is neither deeply explained nor well verified.

Thus, this work conducts a simulation process using process and thermodynamic state model combined with pinch analysis to explore the thermodynamic performance and heat transfer process of basic ORC with 17 pure dry and isentropic working fluid candidates under the condition where the inlet temperature of waste heat ranges from 120 to 200 °C [27] and the following rules are generalized.

- Rule 1: The optimal working fluid satisfies the “double-pinch rules”.

For a basic ORC with the given heat source, the optimal pure working fluid can form the double-pinch points (vaporization Pinch point and preheat Pinch point) with the heat source during their heat transfer in the heat recovery process. This is because the double-pinch state implies a perfect temperature match between the waste heat and working fluid and, thus, reaches a high systematic efficiency of ORC [28].

- Rule 2: The optimal pure working fluid can be determined via a linear relation between the critical temperature of the working fluid and the inlet temperature of the heat source.

$$T_c^{opt} = a \times T_{WH,in} - b \quad (1)$$

where T_c^{opt} is the optimal critical temperature, $T_{WH,in}$ is the waste heat inlet temperature and a and b are constants. It is worthy of noting that this relation is simple and significantly useful for the selection and even design of the working fluids of ORC, because the complex ORC process and thermodynamic model can be omitted; the optimal critical temperature can be determined by only given waste heat inlet temperature [26,28]

- Rule 3: The working fluid with higher critical pressure is preferred when its critical temperatures is similar.

Simulation shows that when the critical temperatures are similar, as the critical pressure increases, the slope of vapor saturation curve and the area surrounded by the saturation curve increase [24], which increases the phase change load and, thus, effectively improves the output of the system [7].

- Rule 4: The ratio of the critical temperature and critical pressure of the optimal working, P_c/T_c should not be more than one.

According to the analysis of the critical temperature and critical pressure of more than 90 working fluids in REFPROP, it is found that the ratio of critical pressure ($\times 10$ KPa) to critical temperature (K), P_c/T_c can be used to distinguish the types of the working fluids. When the ratio is not larger than one, the working fluid is dry and isentropic; otherwise, it is wet. Thus, the ratio should not be more than one to ensure that the selected working fluid is dry and isentropic.

Based on the above-mentioned rules, the optimal working fluid of an ORC can be easily selected from the existing working fluids. In addition, new working fluid can also be effectively designed for the actual waste heat recovery process by using the CAMD technique without the consideration of the complex process and thermodynamic model of ORC according to the above rules.

2.2. Simplified CAMD Model for the Design of Working Fluid

The design model of optimal working fluids based on the above quantitative selection rules about the critical properties of working fluids for a given waste heat source is established in this section. In the established model, the ORC process and thermodynamic state models are replaced by the quantitative selection rules, so the complex nonlinear terms can be effectively reduced.

2.2.1. Objective Function

The objective function is to minimize the difference between the critical temperature of the designed working fluid and the optimal critical temperature for a given waste heat source, since the critical temperature of the working fluid is regarded as the most important factor for working fluid selection [24].

$$\min (T_{cm} - T_c^{opt})^2 \quad (2)$$

where T_{cm} is the critical temperature of the designed mixture working fluid.

2.2.2. Constraints

The optimal critical temperature is determined by the inlet temperature of the heat source, which is shown in Equation (1). To ensure that the designed working fluid is dry and isentropic and, at the same time, guarantees the output of the system, the following equation is introduced according to rules 3 and 4.

$$\sigma \leq r = \frac{P_{cm}}{T_{cm}} \leq 1 \quad (3)$$

where P_{cm} is the critical pressure of the designed mixture working fluid and σ is a constant. The greater the value of σ is, the greater the critical pressure of the designed working fluid and the better the performance of the ORC will be.

Structural feasibility constraints, belonging to the constitutive model, include octet rules, group connection feasibility constraints and group number constraints [29], which are given as follows.

$$\sum_k (2 - v_k) n_{i,k} = 2m_i \quad (4)$$

$$\sum n_{i,k} \geq n_{i,j} (v_j - 1) + 2 \quad (5)$$

$$\sum_k n_{i,k} \geq 4(1 - m_i), \forall v_k \geq 2 \quad (6)$$

$$\sum_k n_{i,k} \geq v_j + 1 \quad (7)$$

$$n_k^L \leq n_{i,k} \leq n_{i,k}^U \quad (8)$$

$$n^L \leq \sum_k n_{i,k} \leq n^U \quad (9)$$

where the subscripts i and k indicate the designed molecule and functional group; n represents the number of a function group appearing in the designed molecule and v indicates the valency of the functional group. The superscript L and U stand for the lower and upper bounds. Note that in this model, the integer variable m is used to represent the types of molecule, where m is assigned to be the value of 1, 0, -1 for acyclic, monocyclic and bicyclic molecule [30].

The physical properties of pure working fluids can be predicted by GCM, where the physical properties are determined by the group contribution value and the number of functional groups [29]. The lower and upper bounds of the physical properties of pure working fluids are also given to ensure the rationality of the design.

$$T_{c,i} = \frac{T_{b,i}^p}{0.584 + 0.965 \sum_k n_{i,k} T_{ck} - \left(\sum_k n_{i,k} T_{ck} \right)^2} \quad (10)$$

$$T_{b,i} = 198.2 + \sum_k n_{i,k} T_{bk} \quad (11)$$

$$P_{c,i} = \left(\frac{1}{0.1155 + \sum_k n_{i,k} P_{ck}} \right)^2 + 0.0519 \quad (12)$$

$$V_{c,i} = 14.6182 + \sum_k n_{i,k} V_{ck} \quad (13)$$

$$Z_{c,i} = \frac{P_{c,i} V_{c,i}}{RT_{c,i}} \quad (14)$$

$$P_c^L \leq P_{c,i} \leq P_c^U \quad (15)$$

$$T_c^L \leq T_{c,i} \leq T_c^U \quad (16)$$

$$T_b^L \leq T_{b,i} \leq T_b^U \quad (17)$$

$$V_c^L \leq V_{c,i} \leq V_c^U \quad (18)$$

where $T_{c,i}$ and $T_{b,i}$ are the critical and normal boiling temperatures of pure working fluid, $V_{c,i}$ and $Z_{c,i}$ are the critical volume and critical acentric factor, P_{ck} , T_{ck} and V_{ck} are group contribution values for critical pressure, critical temperature and the critical volume. These physical properties of the mixture working fluids can be calculated from the physical properties of the pure working fluid and its proportion in the mixture [29].

$$\sum_i x_i = 1 \quad (19)$$

$$T_{cm} = \sum_i x_i T_{c,i} \quad (20)$$

$$P_{cm} = \frac{8.314 \sum_i x_i Z_{c,i} T_{cm}}{\sum_i x_i V_{c,i}} \quad (21)$$

$$P_c^L \leq P_{cm} \leq P_c^U \quad (22)$$

$$T_c^L \leq T_{cm} \leq T_c^U \quad (23)$$

It can be seen in the above established model that the model takes the critical property of the designed working fluid as the objective directly and evolves no ORC process and thermodynamic state model, which effectively eliminates most of the complex nonlinear terms and improves the solvability of the CAMD model. It is worth noting that the model established in this section can be used for the design of both the mixture working fluids and pure working fluids. When the number of working fluids is set to 1, the output of the model turns to be the designed pure working fluid.

3. Case Study

3.1. Fundamental Data

The temperature of low temperature generated in industrial processes is usually lower than 473.15 K. In this section, the inlet temperature of waste heat source ranging from 473.15 to 413.15 K is discretized into four scenarios, with a step of 20 °C for working fluid design with the given waste heat. Other fixed parameters, such as the lower and upper bounds of the properties for the designed working fluid and number of functional groups, are summarized in Table 1.

Table 1. The fixed parameters for the design process.

Properties	Units	Lower Bound	Upper Bound
$P_{c,i}, P_{cm}$	bar	10	90
$T_{c,i}, T_{cm}$	K	330	900
$T_{b,i}$	K	250	500
$n_{i,k}$	/	2	15
$T_{WH,in} = 473.15 \text{ K}, 453.15 \text{ K}, 433.15 \text{ K}, 413.15 \text{ K}$			
$a = 0.92917, b = 11.27806, \sigma \geq 0.8$			

For candidate functional groups, a basic set of 39 functional groups is displayed in after careful research and analysis of the existing working fluids in REFPORP [31] and other databases. According to their chemical elements contained, the functional groups are divided into six groups. (see the Table 2)

Table 2. Basic set of candidate functional groups for ORC working fluids.

Carbon Groups	Halogen Groups	Oxygen Groups	Nitrogen Groups	Sulfur Groups	Aromatic Groups
-CH ₃	-F	-OH	-CH ₂ NH ₂	-CH ₂ SH	ACH
-CH ₂ -	-Cl	-CHO	>CHNH ₂	CH ₃ S-	AC
-CH<	-Br	CH ₃ CO-	CH ₃ NH-	-CH ₂ S-	ACCH ₃
>C<	-I	-CH ₂ CO-	-CH ₂ NH-	>CHS-	ACCH ₂
		-COO-	>CHNH-		ACCH
		>CH-O-	CH ₃ N<		ACOH
		-CH ₂ O-	-CH ₂ N<		ACNH ₂
		CH ₃ O-	-CH ₂ NO ₂		ACCI
		-COOH	>CHNO ₂		ACF

All the calculations are carried out on GAMS [32] platform with the solution environment of a Core i5-4460 @ 3.20 GHz 8.00 Gb. SCIP is selected as the solver for the presented CAMD model.

3.2. Results and Discussion

By solving the CAMD working fluid design model established in Section 2.2, the obtained optimal pure working fluids and binary mixture working fluids for different heat source scenarios are summarized in, as well as the existing optimal working fluid. Note that the conventional CAMD model has no feasible solutions returned with any MINLP solver in an acceptable time, whereas the solving times of the modified CAMD model for working fluid design of all scenarios in are all less than 10 s. It indicates that the proposed CAMD model is significantly more effective than the conventional one containing the complex process and thermodynamic state model.

It can be seen from that the existing and designed molecules are mainly hydrocarbon compounds with a carbon chain as the main chain and all compounds contain relatively more halogen elements (i.e., F), which verifies the rationality of the design [33]. This can also be inferred by the designed pure working fluid and mixture working fluids, because they are all dominated by acyclic molecules. However, when the inlet temperatures of the heat source is 473.15 K and 413.15 K, the pure working fluids in binary mixture working fluids contain a monocyclic molecule, which indicates the application potential of cyclic molecules in the design of working fluids and it is necessary to consider the cyclic working fluids for the design of optimal ORC working fluids. It should be noted that, in the proposed CAMD model, the numbers of some elements and functional groups that may suffer environmental and safety problems have been restricted to meet the sustainability requirements in the design of working fluid. However, the chlorinated groups still appear in the designed molecules due to their excellent performance; see the last column in Table 3. It is also a reminder that more stringent environmental assessment indicators and constraints should be added in the CAMD model of working fluids.

Figure 2a shows the differences in critical temperatures between the existing working fluid, the designed pure working fluid and the designed mixture working fluid when compared with the optimal ones in the corresponding four scenarios. It can be seen from Figure 2a that, for the given inlet temperature of waste heat, the critical temperatures of the designed working fluids, no matter pure or mixture, are much closer to the optimal ones in all scenarios, especially for the designed mixture working fluids, whose critical temperatures are exactly the same as the optimal ones in all scenarios. It is likely that the binary mixture working fluid greatly expands the options of ORC working fluids and makes it possible to find the theoretical optimal working fluid for ORCs in each scenario. This further implies that the existing working fluids may fail to well meet the requirement of the given waste heat and, thus, verifies the necessity of the use of the CAMD technique for the design of optimal working fluids for the ORC system.

Table 3. The optimal designed and existing working fluids for the given inlet temperatures of waste heat.

Scenario	$T_{WH,in}$	T_c^{opt}	Working Fluid	
			existing	
S1	473.15	447.7		R245ca ($\text{CHF}_2\text{-CF}_2\text{-CH}_2\text{F}$)
			designed pure	$\text{COO(F)-CN(F}_4\text{)}$
			mixture	0.89154 $\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF(CH}_3\text{)- (monocyclic)}$
				0.10846 $(\text{CH}_3)_2\text{-C(I)-CHClF}$
S2	453.15	429.1		R245fa ($\text{CF}_3\text{-CH}_2\text{-CHF}_2$)
			designed pure	$\text{CH}_3\text{N-CH(F)-CH(F)-CH(F}_2\text{)}$
			mixture	0.20034 $\text{CHNO}_2(\text{Br})\text{-CF}_2\text{-CF}_2\text{-CH}_2\text{SH}$
				0.79966 $\text{CH}_3\text{-CH}_2\text{O-CF}_2\text{-CF}_2\text{-CF}_3$
S3	433.15	410.5		R600A ($\text{CH(CH}_3\text{)}_3$)
			designed pure	$\text{CO(F}_3\text{)-C(F}_2\text{)OF}$
			mixture	0.32451 $\text{CH}_3\text{-CF}_2\text{-CHS(CH}_3\text{)-CH}_3$
				0.67549 $\text{CH}_3\text{-CH(CH}_3\text{)-CF}_2\text{-CF}_2\text{-CHClF}$
S4	413.15	392		RC318 (C_4F_{10})
			designed pure	$\text{CH}_3\text{-CF}_2\text{-CF}_2\text{Cl}$
			mixture	0.89736 $\text{-CH-O(CH}_3\text{)-CF}_2\text{-CF}_2\text{-CF}_2\text{- (monocyclic)}$
				0.10264 $\text{CHClF-CH}_2\text{-CH(CHClF)-CH}_2\text{SH}$

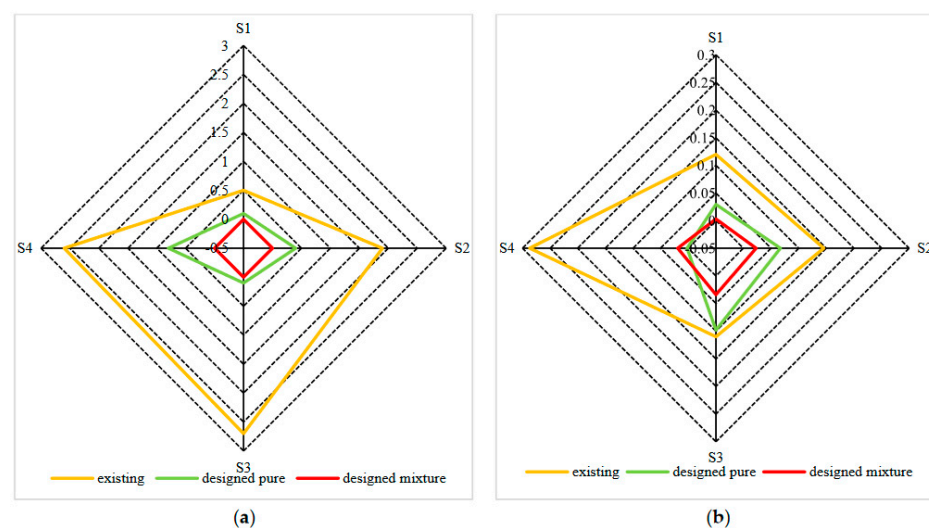
**Figure 2.** The difference in actual and optimal values (a) critical temperature and (b) r value.

Figure 2b shows the differences in the r values among the existing and the designed working fluids when compared with the optimal ones in the corresponding four scenarios. According to rules 3 and 4, the r value of the optimal working fluids is one and the closer the r value of a working fluid to one is, the better performance of the working fluid will be. It can be seen from Figure 2b that the r values of the designed working fluids are closer to one than the existing ones in all scenarios, indicating that the designed working fluids are more isentropic and have better thermodynamic performance than the existing ones. In addition, the r values of the designed mixture working fluids are closest to the optimum, implying the great potential to the application of the mixture working fluids in actual scenarios. Note that in scenario 4, the r values of the designed pure working fluid and the binary mixture working fluid are similar, which is also reasonable because both the pure

and mixture working fluids have the potential to be optimum. In this case, the mixture is still a better option due to its lower irreversible loss.

4. Conclusions

In this work, an effective CAMD-based method for the design of ORC working fluid is proposed. In this method, the influences of the critical properties of working fluids on the ORC performances are first explored and generalized to construct a quantitative relationship between the waste heat sources and critical properties of working fluids. The quantitative relationship is then adopted to target the optimal working fluid by solving a simplified CAMD model for working fluid design. The feasibility of this method is verified via a series of practical cases. Results show that the proposed method can effectively reduce the complexity of the model and improve the feasibility and solvability of the CAMD model. In addition, the designed mixture working fluids feature better thermodynamic performance and can adapt to more design requirements, verifying their great application potential in actual waste heat recovery scenarios. Subsequent work will focus on the integration of the proposed CAMD model with the assessment models of the economy, the environmental impacts and safety, so as to conduct a comprehensive analysis of the designed working fluids.

Author Contributions: Conceptualization, L.K.; methodology, L.K. and J.T.; software, J.T.; validation, L.K. and J.T.; formal analysis, L.K.; investigation, L.K. and Y.L.; resources, J.T.; data curation, J.T.; writing—original draft preparation, J.T.; writing—review and editing, L.K.; visualization, J.T.; supervision, L.K. and Y.L.; project administration, L.K.; funding acquisition, L.K. and Y.L. All authors have read and agreed to the published version of the manuscript.

Funding: The authors gratefully acknowledge funding from the key Research and Development Project of Shaanxi Province (No. 2022GY-185 and No. 2022GY-197) and the projects (No. 22238006) sponsored by the National Natural Science Foundation of China (NSFC).

Conflicts of Interest: The authors declare no conflict of interest.

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