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Evaluation of working fluids for organic Rankine cycles using group-contribution methods and second-law-based models

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Abstract: The group-contribution (GC) methods suffer from a limitation concerning to the prediction of process-related indexes, e.g., thermal efficiency. Recently developed analytical models for thermal efficiency of organic Rankine cycles (ORCs) provide a possibility of overcoming the limitation of the GC methods because these models formulate thermal efficiency as functions of key thermal properties. Using these analytical relations together with GC methods, more than 60 organic fluids are screened for medium-low temperature ORCs. The results indicate that the GC methods can estimate thermal properties with acceptable accuracy (mean relative errors are 4.45%−11.50%); the precision, however, is low because the relative errors can vary from less than 0.1% to 45.0%. By contrast, the GC-based estimation of thermal efficiency has better accuracy and precision. The relative errors in thermal efficiency have an arithmetic mean of about 2.9% and fall within the range of 0−24.0%. These findings suggest that the analytical equations provide not only a direct way of estimating thermal efficiency but an accurate and precise approach to evaluating working fluids and guiding computer-aided molecular design of new fluids for ORCs using GC methods.

Key words: organic Rankine cycles (ORCs); group contribution methods; working fluids; property estimation; computer-aided molecular design

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1 Introduction

Organic Rankine cycles (ORCs) have recently attracted considerable interest because of the urgent need for generating power from low-grade heat sources [1−3]. Low-grade heat sources (e.g., solar heat, geothermal energy, and industry waste heat) differ from high-temperature heat sources in temperature and energy density, with a difference that makes the Rankine cycle use steam inefficient [4−6]. Rankine cycles using organic working fluids (i.e., ORCs) tend to be more appropriate for converting low-grade heat into power [2]. A key aspect of applying ORCs is the selection of an appropriate organic working fluid. In this context, an appropriate organic fluid means that the working fluid is safe, environmentally friendly, and thermodynamically efficient. It is, however, a great challenge to achieve the optimum selection of organic fluids for Rankine cycles because of the diversity of organic fluids, performance criteria, and heat-source characteristics [7−9].

Many studies have been devoted to evaluating and selecting organic fluids for the Rankine cycle [5, 8, 10−28]. Roughly speaking, these studies can be divided into two groups: the first group has used experimentally validated equations of state (EoS) or

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property diagrams (e.g., NIST reference database [29]) to evaluate organic fluids [5, 8, 10]. The previous studies have examined the influence of organic fluids on net power output [30, 31], turbine expansion ratio [32, 33], thermal efficiency [34−36], exergetic efficiency [37−39], minimum superheat degree [40−42], and component sizes [43]. Among these indexes, the greatest interest is the correlations between thermal efficiency of ORCs and critical temperature [44, 45], normal boiling point [46], molecular complexity [47−50], Jacob number [35, 46, 51], figure of merit [46], molar mass [52, 53], acentric factor [54], and reduced ideal gas heat capacity [55]. But, the problem with these studies is that they require complete experimental data to create EoS for the evaluated fluids and thus can only screen a limited list of organic fluids.

By contrast, the second group of the studies employed group-contribution (GC) methods to calculate thermal properties of organic working fluids [11−22, 24−28]. The GC methods are often used in computer-aided molecular design (CAMD) of new fluids for ORCs because they can predict physical and thermal properties without recourse to complete experimental data [14, 15, 18, 19]. HUKKERIKAR et al [21] presented revised and improved GC models for 18 pure components properties. They also analyzed the uncertainties in the estimated property values. A robust method was presented for assessing utilization efficiency (Second Law Efficiency) of ORCs plants based on molecular group contribution methods in Ref. [24]. BROWN et al [12, 13] combined P-R EoS and GC methods to evaluate the performance properties for well-described and not-so-well- described working fluids in ORC. They only compared these physical properties of working fluids for ORCs. These thermal parameters were not systematically compared with the NIST database, in which these parameters are important for the evaluation of working fluids in ORCs. MARTIN et al [18] and WHITE et al [19] proposed an optimization framework by combining GC methods, SAFT-γ Mie EoS with an ORC power system to select working fluids based on hydrocarbon function groups. LAMPE et al [25, 27] provided an approach to select working fluids and optimize the process for ORCs, underlying the PC-SAFT EoS in a continuous-molecular targeting approach (CoMT-CAMD). Unlike LAMPE et al thought that the ORC system is tailored to the specific application, PALMA-FLORES et al [26] presented a new approach that can design novel fluids by using PC-SAFT with GC methods. But these studies in Ref. [25−27] are limited in a low-temperature heat source for ORC system. A methodology was developed to estimate the process-related properties of the generated working fluids for ORCs based on GC methods and Peng-Robinson (P-R) EoS in Refs. [14, 15, 28]. However, the above models, in which the required properties are calculated by combining EoS with GC methods, are able to produce iterative calculation. The involved iterative calculation is a more complicated process and is adverse to the evaluation of working fluids' application for ORCs. These predicted thermal properties are considered an objective parameter to select organic fluids. However, the screened fluid only determined by GC methods may not be the one that has the best thermal performance in a cycle. The thermal performance of a cycle depends, not only on GC methods, but on many other parameters (such as *Ja* number) for design and optimization. Therefore, it would be of interest and useful to develop a method that can predict performance indices of ORCs based on properties yielded by GC methods. Such a method can not only screen a wide range of organic fluids but predict indices relating directly to ORCs, overcoming the disadvantages of EoS.

The purpose of this paper is to report a method that evaluates the thermodynamic performance of ORCs using the thermal properties obtained from GC methods. To achieve this purpose, we develop a set of analytical solutions for work and thermal efficiency of ORCs, which is of satisfactory accuracy and enables us to calculate work and thermal efficiency using thermal properties given by GC methods. This method is validated by screening more than 60 organic fluids that are available in the NIST reference database. The comparison shows that the GC-based methods can estimate work and thermal efficiency with relative errors within 10.8% and 2.9%, smaller than those of thermal properties.

2 System description and modeling

2.1 Analytical models for ORCs

Figure 1 shows single organic Rankine cycle in *T*–*s* diagrams. As can be seen, a Rankine cycle works in subcritical conditions and requires several numbers of components, which includes isentropic compression in a pump, constant pressure heat addition in an evaporator, isentropic expansion in a turbine, and constant pressure heat rejection in a condenser. The working fluid is isentropically compressed in the pump (1−2) and flows into the heat exchangers to take the available energy from the heat source (2−5). Then the highest temperature of the fluid is reduced in the turbine to produce mechanical power, which is transformed into electricity through a generator (5−6s). To close the loop, the fluid is condensed and pumped again (6s−1). Conventionally, the work and thermal efficiencies of an ORC are calculated by enthalpies of state points (Figure 1), a method that requires high-accuracy EoS or property diagrams. A major problem with GC methods is that they cannot yield enthalpies and thus work and thermal efficiency. To overcome this problem, we developed several analytical equations for work and thermal efficiency that are functions of operating temperatures and several thermal properties of the working fluid. These explicit equations can extend the prediction ability of GC methods, without recourse to EoS.

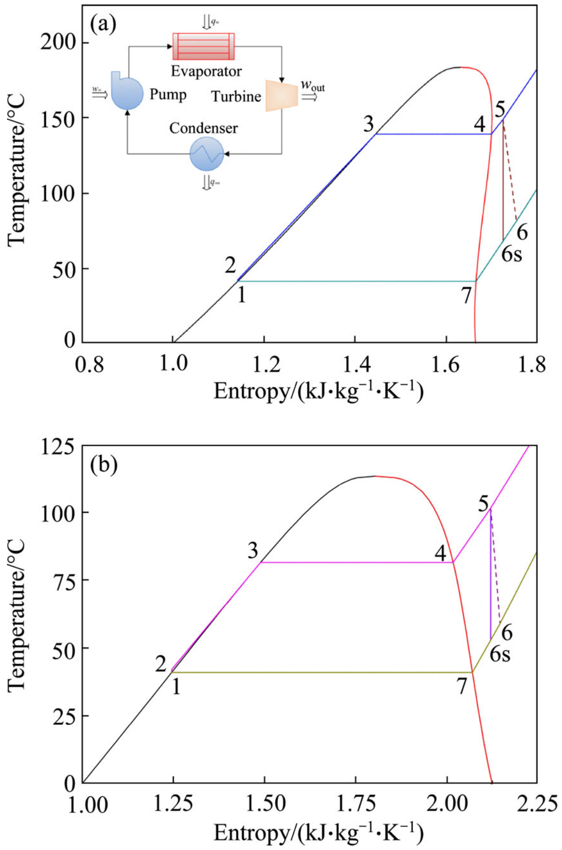

Figure 1 Organic Rankine cycle represented in temperature−entropy (*T*–*s*) diagrams: (a) A Rankine cycle using a dry fluid (d*s*/d*T*>0); (b) A Rankine cycle using a wet fluid (d*s*/d*T*<0)

These analytical equations can be derived from a rigorous entropy-generation analysis of ORCs and have been published elsewhere [56]. Thus only final expressions are summarized here. For the ORC shown in Figure 1, the thermal efficiency can be determined by Eq. (1):

$$\eta=\eta_t\eta_{\mathrm{C}}\left[1-\frac{1-\eta_{\mathrm{C}}}{2}\frac{Ja+\dfrac{c_{p,1}\left(T_3-T_1\right)}{r}\left(\dfrac{T_3}{T_1}\right)^2\tau^2-Ja_s\lambda}{1+Ja+Ja_s}\right] \tag{1}$$

where

$$Ja=\frac{c(T_3-T_1)}{r} \tag{2}$$

$$Ja_{\mathrm{s}}=\frac{c_p(T_5-T_3)}{r} \tag{3}$$

$$\lambda=\frac{T_5-T_3}{T_3-T_1} \tag{4}$$

$$\tau=\frac{T_{6\mathrm{s}}-T_1}{T_3-T_1}=1-\frac{\overline{r}\overline{\beta}}{\overline{c}_p} \tag{5}$$

where r is the latent heat of evaporation of the working fluid at the evaporating temperature T_3; c, c_p, $c_{p,1}$ are the average heat capacity during the preheating process 2−3, the superheating process 4−5 and the desuperheating process 6s−7, respectively; η_{C} denotes the Carnot efficiency: $\eta_{\mathrm{C}}=(T_3-T_1)/T_3$; $\overline{c}_p$, $\overline{r}$, $\overline{\beta}$ are the averages of c_p, r, and volumetric expansion coefficient of saturate-vapor from T_1 to T_3, which can be well approximated by the values at $(T_1+T_3)/2$.

Equation (1) is very general but somewhat complicated; it is desirable to simplify Eq. (1) according to the feature of working fluids. Organic fluids fall into three categories: dry, wet, and isentropic fluids in terms of the slope of the saturated vapor curve in the *T*–*s* plane (Figure 1). If a dry fluid is used in medium-low temperature ORCs, superheating 4−5 may be unnecessary or insignificant. In this case, Eq. (1) reduces to follows:

$$\eta\approx\eta_t\eta_{\mathrm{C}}\left[1-\frac{1-\eta_{\mathrm{C}}}{2}\frac{Ja+\dfrac{c_{p,1}\left(T_3-T_1\right)}{r}\left(\dfrac{T_3}{T_1}\right)^2\tau^2}{1+Ja}\right] \tag{6}$$

For wet fluids, desuperheating 6s−7 is generally unnecessary (Figure 1(b)), and Eq. (1) becomes

$$\eta \approx \eta_t \eta_\mathrm{C}\left(1-\frac{1-\eta_\mathrm{C}}{2}\frac{Ja-Ja_\mathrm{s}\lambda}{1+Ja+Ja_\mathrm{s}}\right) \tag{7}$$

For isentropic fluids, the entropy generation of desuperheating 6s−7 is usually offset by the superheating 4−5. Therefore, Eq. (1) reduces to the following extremely simple form:

$$\eta \approx \eta_t \eta_\mathrm{C}\left(1-\frac{1-\eta_\mathrm{C}}{2}\frac{Ja}{1+Ja}\right) \tag{8}$$

The work produced by the turbine is the difference in vapor enthalpy between inlet and outlet states, and can be approximated by Eq. (9):

$$w_\mathrm{out} = \eta_t \eta_\mathrm{C}\left\{r+\frac{\eta_\mathrm{C}T_3}{2}\left[c\left(1+\eta_\mathrm{C}\right)+c_p(2\lambda+\frac{T_1}{T_3}\lambda^2)-\frac{c_{p,1}T_3}{T_1}\tau^2\right]\right\} \tag{9}$$

2.2 Group-contribution methods

A GC method is a computational model which estimates physical and thermodynamic properties of pure components by summarizing the contributions of simple groups that form the molecules [21]. Once the contribution of a functional group is determined, it remains unchanged and is transferable between different molecules. GC methods can quickly estimate properties with few computational resources [22]; thus, they are the most widely used property prediction method. Various GC models have been developed for estimating thermodynamic properties. The following summarizes the models used in this work.

The GC^+ models proposed by HUKKERIKAR et al [21] were used for estimating critical temperature T_c, critical pressure P_c, and acentric factor ω.

$$T_\mathrm{c} = T_\mathrm{c0}\ln\left(\sum_i N_i C_i + w\sum_j M_j D_j + z\sum_k O_k E_k\right) \tag{10}$$

$$P_\mathrm{c} = P_\mathrm{c1}+\left[\left(\sum_i N_i C_i + w\sum_j M_j D_j + z\sum_k O_k E_k\right)+P_\mathrm{c2}\right]^{-2} \tag{11}$$

$$\omega = \frac{\omega_\mathrm{a}}{\omega_\mathrm{b}}\ln\left[\left(\sum_i N_i C_i + w\sum_j M_j D_j + z\sum_k O_k E_k\right)+\omega_\mathrm{c}\right] \tag{12}$$

where T_c0, P_c1, P_c2, ω_a, ω_b, ω_c are values of the universal constants for the properties: T_c0= 181.6738 K, P_c1=0.0519 bar, $P_\mathrm{c2}^{-0.5}$=0.1155 $\mathrm{bar}^{-0.5}$, and ω_a=0.9132, ω_b=0.447, ω_c=1.0039; N_i, M_j, O_k denote the number of i, j, k groups in the molecule; C_i, D_j, E_k are group-contribution values for the considered group.

The GC model for the enthalpy of vaporization is a function of the reduced temperature T_r [57]:

$$r=\sum_j N_j\left[a_j(1-T_\mathrm{r})^{1/3}+b_j(1-T_\mathrm{r})^{2/3}+c_j(1-T_\mathrm{r})\right] \tag{13}$$

where the reduced temperature T_r is defined as T/T_c; N_j denotes the number of j group in the molecule; a_j, b_j, c_j are group-contribution values for the considered group; the unit of r is kJ/mol.

The used GC model for the ideal gas heat capacity is [58]:

$$C_p^0=\sum_k N_k a_k-37.93+\left(\sum_k N_k b_k+0.21\right)T+\left(\sum_k N_k c_k-3.91\times10^{-4}\right)T^2+\left(\sum_k N_k d_k-2.06\times10^{-7}\right)T^3 \tag{14}$$

where N_k denotes the number of k group in the molecule; a_k, b_k, c_k, d_k are group-contribution values for the considered group.

The liquid heat capacity, related to the ideal gas capacity at the same temperature, can be estimated by the following expression [59]:

$$C_p^l=C_p^0+R\left\{1.45+\frac{0.45}{1-T_\mathrm{r}}+\omega\left[4.2775+\frac{6.3(1-T_\mathrm{r})^{1/3}}{T_\mathrm{r}}+\frac{0.4355}{1-T_\mathrm{r}}\right]\right\} \tag{15}$$

where T_r denotes reduced temperature, $T_\mathrm{r}=T/T_\mathrm{c}$; R is gas constant. All the group-contribution values occurring in these models can be found in the literature, thus they are not repeated here.

3 Results and discussion

More than 60 organic fluids are screened as candidates for ORCs, including dry, wet, and isentropic fluids. Before examining the performance of ORCs, we compared the thermodynamic properties calculated by the GCMs and those calculated by the NIST reference database [29], because we found research has not yet systematically validated GC methods in the ORCs field (including the refrigeration field). In Figures 2−5, the two gray lines represent the relative errors of −10% and 10%, respectively.

3.1 T_c and P_c

Figure 2 compares critical temperature and pressure (T_c and P_c) calculated by the GC methods (GCM) and the NIST database for the selected working fluids. The comparison shows that the agreement of T_c is slightly better than P_c. Compared to NIST, the predictions of T_c by the GC methods have an average relative error smaller than 5.0% and those of P_c have an average relative error smaller than 10.0%. Among the screened fluids, only 9 working fluids have relative errors in T_c exceeding 10.0%, but 20 fluids have relative errors in P_c exceeding 10.0% (Figure 2). The maximum relative errors in T_c and P_c are slightly larger than 30.0% and 40.0%, respectively.

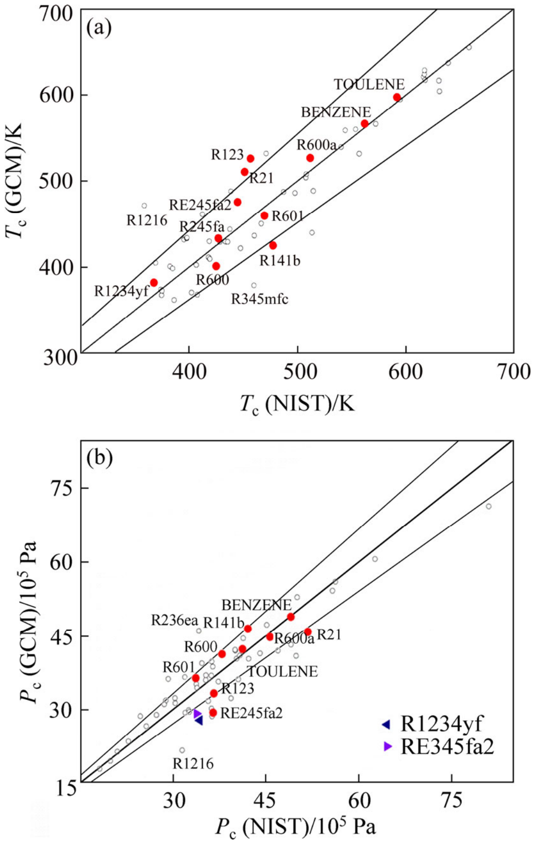

Figure 2 Comparison of T_c (a) and P_c (b) calculated by NIST and GCM

3.2 r and c

The latent heat of evaporation r and the heat capacity of the saturated liquid c are most relevant to the evaluation of working fluids for ORCs. It is generally desirable to use in ORCs an organic fluid having a relatively large r and small average c [3, 43, 53]. For a given T_1 and T_3, Figure 3 compares r and c calculated by the NIST database and the GC methods. Again, Figure 3 shows a contrast between r and c: the average errors of the prediction of r and c are 5.85% and 11.5%, respectively; and only 11 organic fluids have relative errors in r larger than 10.0%, but 30 fluids have relative errors in c exceeding 10.0%. Unlike T_c, P_c and r, c given by the GC methods tends to be smaller than that given by the NIST data, implying that the GC models for c may involve systematic bias in c (Figure 3).

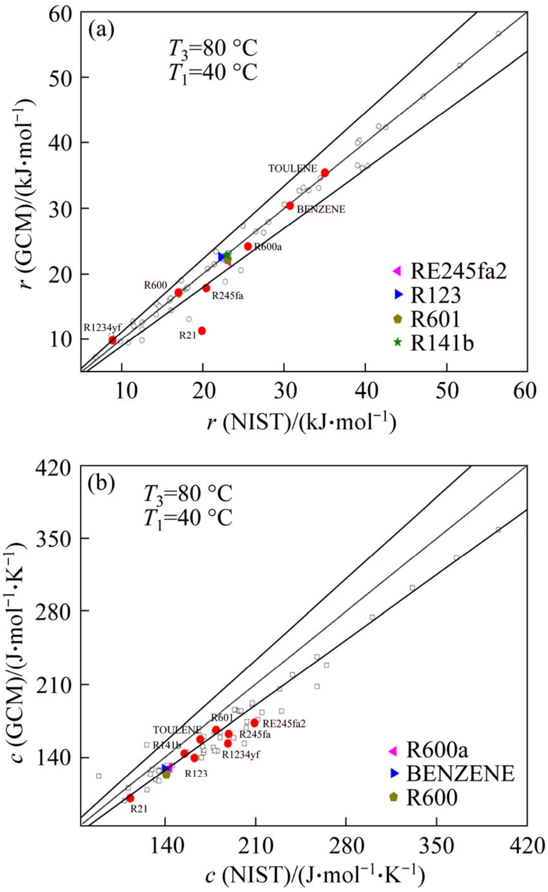

Figure 3 Comparisons of r (a) and c (b) calculated by NIST and GCM

The systematic bias of c contributes accordingly to the systematic bias in c/r (Figure 4). The average relative errors in c/r fall within a range of 0.75%−55.6% with an average error about 12.0%. The quantity c/r contains key thermodynamic information of a working fluid [60, 61] and may be the most important parameter for screening working fluids. In conjunction with T_1 and T_3, c/r has been used to define the dimensionless variable Ja number.

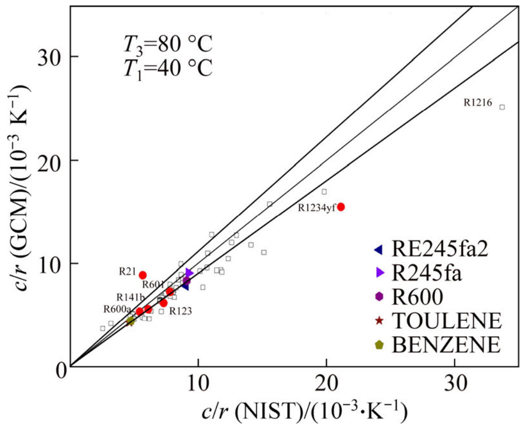

Figure 4 Comparison of c/r calculated by NIST and GCM

Therefore, the estimate of c/r is even more important than the estimates of other properties. From the preliminary study, it can be concluded that while the relative error is slightly larger than those of c and r, the estimate of c/r from the GC method is still acceptable for most organic fluids.

3.3 w_{out} and η

The problem with the GC methods is that they can only predict physical and thermodynamic properties of working fluids and fail to predict the thermodynamic performances of ORCs, such as work and thermal efficiency, because the GC methods cannot estimate enthalpy. The present authors have developed a set of explicit equations for these two performance indexes by a rigorous entropy-generation analysis of ORCs [56]. These equations express the work and thermal efficiency as analytical functions of evaporating and condensing temperatures, as well as key thermal properties (not the state variable enthalpy). Having these equations, we can determine w_{out} and η directly using the properties estimated by the GC methods (referred to as GC-based method hereafter).

Figure 5 compares the work w_{out} and the thermal efficiency η estimated by the GC-based method with those given by the NIST database (enthalpies were calculated first). As shown in Figure 5(a), w_{out} given by the GC-based method tends to be greater than the counterpart yielded by the NIST database, namely, there is a systematic bias in the prediction of w_{out}. The relative error of w_{out} is within the range of 0.18%−33.9%, and the average error is slightly larger than 10.0%. But, the accuracy and precision of the estimation of η are surprisingly high (Figure 5(b)). For the given T_1 and T_3, the GC-based approach yields thermal efficiency with an average relative error of 3.0%. Among the screened fluids, the prediction for R227ea has the maximum relative error (≈24.0%), and only 3 organic fluids have relative errors exceeding 10.0%. Some reasons for these fluids with larger relative errors are as follows: on one hand, the analytical expressions for the thermal efficiency of ORCs yield relative error; on the other hand, these parameters (such as T_c, P_c, r and c) evaluated by GC methods have different errors for different compounds, especially for sample or symmetrical compounds such as R21 (Ja≈40%) or R227ea (η≈24%).

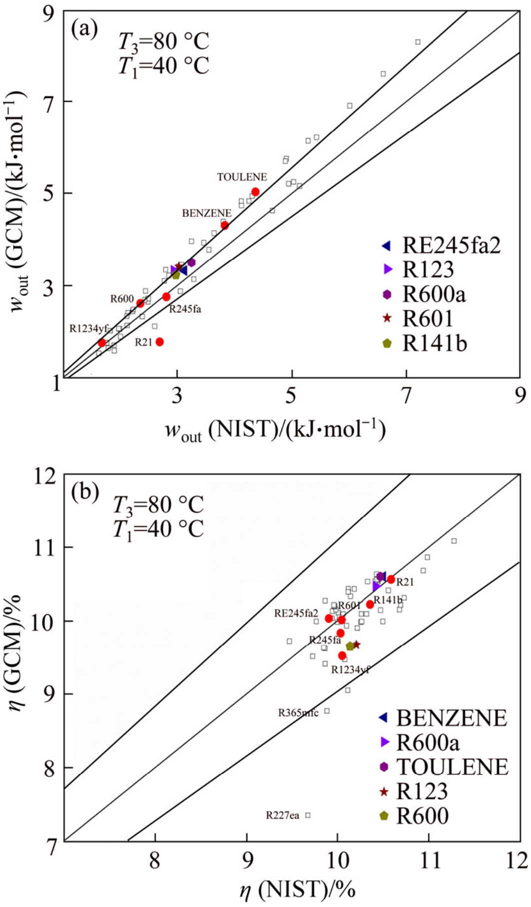

Figure 5 Comparisons of w_{out} (a) and η (b) calculated by NIST and GCM

The high accuracy and precision of the prediction of η can greatly facilitate the application of GC methods in computer-aided molecular design (CAMD). The GC methods are particularly useful in CAMD because they can predict physical properties of pure components with high computational efficiency [18, 27]. Generally, the CAMD identifies an optimum molecular structure for an ORC using some physical or thermal properties as performance measures [14, 15]. As shown above, although the GC methods can estimate thermal properties for most organic fluids with an acceptable accuracy (<10−15%), these estimated properties should be used with caution because the maximum relative error can be as large as 30%−40%. The wide variability in the property estimation, without a doubt, may lead to non-optimal molecular design from the property-based optimization. From this viewpoint, using the estimated η as the objective function can reduce the uncertainty in CAMD because of the high accuracy and precision of the estimation of η.

Moreover, compared with the use of fluid properties, it should be more appropriate to use η as the performance measures in CAMD. On one hand, thermal efficiency is the direct measure of the thermodynamic performance of ORCs, which depends on many properties instead of one (see Eq. (1)). On the other hand, using η can greatly simplify the optimum problem involved in CAMD. First, it can simplify the objective function. In a conventional CAMD, various properties are included in the objective function used in a multi-objective optimization problem, e.g., heat capacity, vaporization enthalpy, etc. Second, since the thermal efficiency can be determined directly from the estimated properties, this approach can further simplify the process-related simulation of ORCs, which is necessary in a CAMD.

4 Conclusions

This paper suggests a set of analytical expressions for the thermal efficiency of ORCs. These analytical expressions, together with GC models for thermal properties, can greatly facilitate the screen and evaluation of working fluids for ORCs. Using the GC methods, several key thermal properties (including T_c, P_c, r and c) can be predicted for more than 60 organic fluids. The screen work reveals that the used GC methods can yield acceptable accuracy for these properties; the average relative errors fall within the range of 4.45%−11.50%. But the precision of the prediction is somewhat low because the variability in the relative errors can be large (from less than 0.1% to 45.0%).

By contrast, the prediction of thermal efficiency has better accuracy and precision than those of thermal properties. The average relative error in η is about 2.9% compared with those given by the NIST database, and the variability of the errors is within the range of 0−24.0%. In fact, only the predictions of 3 fluids have relative errors in η exceeding 10.0%. Based on the results, we inferred that direct estimation of thermal efficiency using the properties given by the GC methods appears to be a reliable approach to evaluating working fluids and guiding computer-aided molecular design of new fluids for ORCs.

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中文导读

基于基团贡献法和热力学第二定律模型对有机朗肯循环(ORCs)工质的评估

摘要：基团贡献(GC)法一般用于预测有机物的热力学属性参数，但对过程指标的预测能力有限，如热力循环过程的效率。本文发展了一种结合 GC 法和有机朗肯循环(ORC)热效率解析模型的方法，可以高效快速地估算有机朗肯循环的热效率，从而在某种程度上克服 GC 方法的局限性。利用 GC 法与 ORC 热效率解析模型，筛选了 60 多种用于中低温有机朗肯循环的有机工质。首先，运用 GC 方法预测了 60 多种有机工质的临界温度 T_c，临界压力 P_c，潜热 r，液体的定压比热容 c 等热力学属性。其次，基于由热力学第二定律推得的 ORC 解析模型，可直接由 GC 法预测的热力学参数直接确定 ORC 的输出功 w_{out} 和热效率 η 等性能指标。计算结果表明，与 NIST 数据相比，本文采用的 GC 模型具有足够的精度来估算热力学参数(T_c，P_c，r，c，w_{out}，η 的平均相对误差分别为 4.45%，9.29%，5.85%，11.5%，10.8%，2.9%)。其中热效率的平均相对误差最小(约为 2.9%)，且所有预测值的误差在 0~24%的范围内。本研究表明 GC 方法与 ORC 解析模型结合，不仅提供了一种估算热效率的直接方法(无需状态方程)，并且提供了一种快速准确的方法来评估有机工质的热力学性能。本文研究成果也为指导基于 GC 法的 ORC 有机工质计算机辅助设计提供借鉴。

关键词：有机朗肯循环；基团贡献法；工质；属性估算；计算机辅助设计