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TOWARDS FREE-CONSTRUCTION OF THERMODYNAMICS CYCLE: A NEW PERSPECTIVE ON WORKING FLUID SELECTION

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ABSTRACT

Over the past two centuries, the research on working fluids drove the tremendous progress of organic Rankine cycle to convert medium- and low-temperature heat into power efficiently. With the increasingly stringent requirements on working fluids, the search for alternative working fluids is a never-ending task. In the present work, a comprehensive review of working fluids selection of ORC is presented to summary the current research results, find out the issues and guide the future developments. The research of working fluid selection is divided into three stages according to research method firstly. Then, the research progress of each stages is summarized. In addition, the research challenges and recommendations for further research of working fluids selection and even for novel thermodynamic cycle are highlighted as well. The results show that for traditional ORC, the optimal working fluid could be selected almost by key parameters such as critical temperature, acentric factor and Jacob number, etc. More importantly, the development direction of novel thermodynamic cycle is presented.

Keywords: organic Rankine cycle, working fluid selection, critical temperature, Jacob number

NONMENCLATURE

Abbreviations	
ORC	organic Rankine cycle
Symbols	
c	specific heat capacity
Ja	Jacob number
r	latent heat
s	entropy
T	temperature
W	work
wf	working fluid
η	efficiency
β	the slope of working fluid saturated liquid line in *T*-*s* diagram
ω	acentric factor
Φ	flow coefficient
ψ	loading coefficient
α_V	volume expansion coefficient
ρ	density
Subscripts and superscripts	
Carnot	Carnot cycle
c	condensation
cr	critical point
com	component
e	evaporation
exp	expander
hse	heat source
max	maximum
m	arithmetic mean
net	net output
ORC	organic Rankine cycle
pump	working fluid pump
P	pressure
r	reduced by critical point
1st	The first law of thermodynamics

1. INTRODUCTION

Since the invention of organic Rankine cycle (ORC), which has been widely studied in the field of medium-

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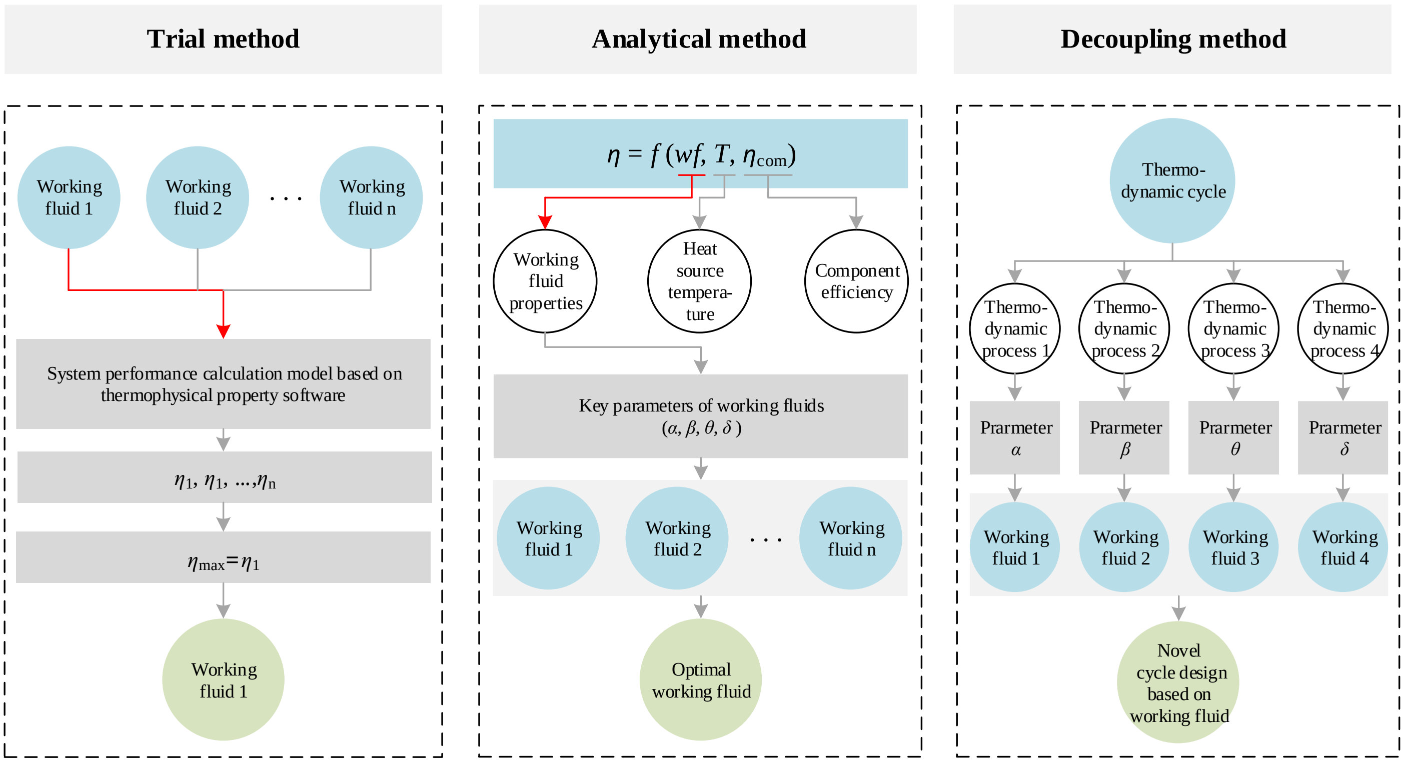

Fig 1 Diagram of research methods for working fluid selection

and low-temperature energy utilization [1], the selection of working fluids has always been a research hotspot. This is mainly because that the actual thermodynamic cycle must rely on working fluids to transfer and convert energy. However, according Carnot cycle, the upper limit thermodynamic cycle efficiency is determined only by the temperature of heat sink and heat source [2]. Based on the Carnot cycle, the thermophysical properties of working fluid in actual ORC are considered. In addition to the limitation of the thermophysical properties on the efficiency of actual ORC, the working fluid could also cause irreversible losses in the actual ORC, such as the finite potential difference in the process of energy transfer and transformation (including temperature difference, pressure difference, concentration difference, etc.) and the irreversible losses caused by dissipation effects (including friction, heat dissipation, leakage, etc.) [2]. Therefore, working fluid is the main reason for the huge performance gap between Carnot cycle and actual ORC. Naturally, the selection of suitable working fluids is one of the basic tasks for the development of ORC.

Many studies were devoted to the selection of working fluids of ORC. There are also several articles presented a general overview at that time. Chen [3], Bao [4], Zhou [5] and Xu [6] presented review researches in relation to the selection of working fluids of ORC respectively, which were categorized according to cycle structure, type of working fluid, operating condition and application scenario. These review papers comprehensively summarized the research progress at that time. And the thermophysical properties of working fluid, stability of working fluid, safety, cost and environmental aspects are considered as the main factors of working fluid selection.

Actually, in recent years, with the deepening of researchers' understanding of the problem, great changes have taken place in the selection of working fluids from the perspective of research method. As shown in Fig 1, the selection of working fluids has gone through three stages using trial method, analytical method and decoupling method respectively. In this paper, the research progress and results of working fluid selection in each stages are summarized and analyzed comparatively. And the current development issues and future directions are also presented. The summary in this paper could promote the understanding of working fluid selection research from the methodological point of view and could also be considered as a research methodology guideline for the construction of thermodynamic cycle. The full-text is shrunken due to page limitation.

2. TRIAL METHOD

The trial method is the original method to be used, which relies heavily on the software for calculating the thermophysical properties of working fluid, such as EES, REFPROP, Coolprop, etc. According to this method, the efficiency of all candidate working fluids should be calculated based on the established ORC thermodynamic model, and the working fluid with highest efficiency or maximum output work would be regarded as the optimal working fluid. As more and more candidate working fluids are considered, some studies attempt to summarize the key thermophysical parameters affecting cycle performance by statistical methods. Xu et al. [7] presented the relationship between critical temperature, heat source temperature and thermal efficiency of ORC based on the analysis of 57 working fluids. 37 working fluids were compared and analyzed by Zhai et al. [8] and the suitable working fluid were recommended according the relationship between critical temperature, heat source temperature and evaporation temperature. The similar conclusions were also concluded by Vivian et al. [9] according the calculation results from 32 working fluids. Wang et al. [10] analyzed 21 working fluids and found the relationship between Jacob number (*Ja*, which is defined as the ratio of sensible heat to latent heat in heat transfer process of working fluid), critical temperature and thermal efficiency. What's more, the quantitative expression between critical temperature and thermal efficiency under constant operation conditions was proposed, as shown in formula (1). The determination coefficient R^2=0.9988. The quantitative expression between critical temperature, acentric factor, heat source temperature and net output work was proposed by Zhao et al. [11], as shown in formula (2). The determination coefficient R^2=0.967548. It is noteworthy that the condensation temperature remained

Table 1 Summary of thermal efficiency equations of ORC

Authors	Year	Functions	Description
Liu et al. [12]	2004	$\eta_{1st}=1-\left[\left(\frac{nT_{rm}}{1-T_{rm}}+1\right)\left(\frac{T_{r\_e}-T_{r\_c}}{T_{rm}}\right)\left(\frac{1-T_{rm}}{1-T_{r\_c}}\right)^n+\left(\frac{1-T_{r\_e}}{1-T_{r\_c}}\right)^n\right]^{-1}$, $T_{r\_m}=\left(T_{r\_e}+T_{r\_c}\right)/2$	Based on the Watson formula [22] describing the latent heat of vaporization working fluids. n is suggested to be 0.375 or 0.38. η_{exp}=100%., η_{pump}=100%.
Mikielewicz et al. [13]	2010	$\eta_{1st}=1-\frac{r_c}{Ja_e\eta_{Carnot}r_e+r_e}$	This formula shows high accuracy for isentropic working fluids. η_{exp}=100%, η_{pump}=100%.
Kuo et al. [14]	2011	$FOM=Ja_e^{0.1}\left(\frac{T_c}{T_e}\right)^{0.8}$	The thermal efficiency of ORC decreases with the increase of *FOM*. η_{exp}=100%, η_{pump}=100%.
Wang et al. [15]	2012	$\eta_{1st}=1-\frac{\ln(T_e/T_c)\times(T_e/T_c-1)^{-1}+(Ja_eT_e/T_c)^{-1}}{1+Ja_e^{-1}}$	η_{exp}=100%., η_{pump}=100%.
He et al. [16]	2014	$\eta_{1st}=\frac{\eta_{Carnot}+\frac{Ja_e}{2}\ln\frac{1}{1-\eta_{Carnot}}}{1+Ja_e}\eta_{exp}$	η_{pump}=100%.
Li et al. [17]	2016	$\eta_{1st}=\eta_{exp}\eta_{Carnot}\left[1-\frac{1-\eta_{Carnot}}{2}\frac{cT_e}{r_e}\left(\frac{1}{\eta_{Carnot}}+\frac{cT_e}{r_e}\right)^{-1}\right]$	This formula was derived for isentropic working fluid using entropy-generation analysis. η_{pump}=100%.
Javanshir et al. [18]	2016	$\eta_{1st}=\eta_{exp}\frac{Ja_e+1-\frac{Ja_e\ln(T_e/T_c)}{T_e/T_c-1}+\frac{1}{T_e/T_c}}{Ja_e+1}$	This formula shows high accuracy for isentropic working fluids. η_{pump}=100%.
Wang and Chen et al. [10, 21]	2017	$\eta_{1st}=1-\frac{T_c}{T_e}(1+Ja_e)/\left[1+\frac{T_e+T_c}{2T_e}Ja_e\right]$	This formula was deduced based on the cycle separation. η_{exp}=100%, η_{pump}=100%.
Xu and Su et al. [19, 20]	2018	$\eta_{1st}=1-\frac{T_c}{T_e-\frac{1}{2\beta\Delta s_e}(T_e-T_c)^2}$	This formula was deduced based on the graphical analysis in *T-s* graph. η_{exp}=100%, η_{pump}=100%.

unchanged in this study, so the heat sink temperature was not involved in the expression of output work.

$$\eta_{\mathrm{ORC}} = -4\mathrm{E}^{-6} \cdot T_{\mathrm{cr}}^{\;2} + 0.0025 T_{\mathrm{cr}} - 0.1467 \quad (1)$$

$$W_{\mathrm{net}} = 0.00215691 \cdot T_{\mathrm{cr}}^{\;1.135539} \cdot \omega^{0.313906} \cdot T_{\mathrm{hse}}^{\;2.742975} \quad (2)$$

In summary, using the method of combining trial calculation with inductive fitting, a conclusion has been reached that the critical temperature could be regarded as the main index and Jacob number, acentric factor could be regarded as the auxiliary indexes for working fluid selection. When there are fewer candidate working fluids and available software for calculating thermophysical properties with high accuracy, the trial method shows advantages of simple and convenient. However, the mechanism of the effect of thermophysical properties on cycle performance is not well anatomized because the thermodynamic model of ORC is a kind of black box model.

3. ANALYTICAL METHOD

In view of the desire for mechanism, more and more scholars tend to select working fluids using analytical method. The three kind of factors affecting the thermal efficiency of thermodynamic cycle could be summarized as the temperature of heat source and heat sink, the thermophysical properties of working fluid and the efficiency of components. In this method, the temperature of heat source and heat sink are usually fixed, and the efficiency of components are usually set to 100%. Then the relationship expression between the thermophysical properties of working fluid and the thermal efficiency of thermodynamic cycle could be deduced using entropy analysis method, graphical analysis method, etc. And the key thermophysical parameters affecting the performance of ORC could be found in expression. Finally, the optimal working fluid could be selected according the key thermophysical parameters.

The thermal efficiency expressions of actual ORC are listed in Table 1. From the formulas in the table above, we could conclude that the key thermophysical parameters of working fluid are latent heat, liquid specific heat, Jacob number and the slope of working fluid saturated line in *T-s* diagram. However, no identical expression has been obtained by different studies due to the difference of heat source and heat sink temperature and different hypothetical conditions in each study. What's more, there are even obvious inconsistent conclusions. According to the researches from Xu et al. [20], the working fluids with high latent and low specific heat show better performance. On the contrary,

Table 2 Summary of researches on the effect of thermophysical properties on thermodynamic Process

Authors	**Year**	**Process**	**Conclusion**
Zheng et al [24]	2013	Heat transfer process	The parameter σ was proposed for the selection of zeotropic working fluid.
Lio et al. [25]	2016	Expansion process	$\eta_{\mathrm{exp}} = f(\Phi, \Psi, R, SP, VR, wf)$ was derived. Thermophysical properties of working fluid are the key parameters affecting the efficiency of expander.
Stijepovic et al. [26]	2012	Expansion process	The isobaric heat capacity, molecular weights and compressibility factor of working fluids were regarded as key factors affecting the performance of expansion process
Burugupally et al.[27]	2019	Expansion process	The efficiency of expander increases with the increase of specific heat ratio of working fluid.
Xu et al. [28]	2017	Compression process	The isentropic efficiency of compression process decreases with the increment of $\alpha_V/\rho c_p$ of different working fluids.

Yamamoto et al. [23] proposed that the candidate working fluids must have low latent heat, which would increase the turbine inlet mass flow rate and give the best operating condition. The reason for this contradiction is that different thermodynamic processes require different working fluids and the hypotheses of thermodynamic process are different in these two researches. This contradiction cannot be solved by taking thermodynamic cycle as the research object.

4. DECOUPLING METHOD

By dividing the thermodynamic cycle into thermodynamic processes, the selection of working fluids for each process is carried out. In this kind of research, if relying on the thermodynamic cycle, the thermodynamic process that has not been studied will be set as the ideal thermodynamic process usually. Besides, the thermodynamic process could also be modeled, simulated or experimented separately.

At present, only a few papers focus on the selection of working fluid for thermodynamic process. Table 2 listed the basic information and main conclusions of such studies. The results show that the conclusions of different studies are quite different for the same thermodynamic process, such as expansion process, which may due to the different types of expanders studied in different researches. Overall, no unified criterion of working fluid selection for each thermodynamic process has been concluded at present. Even so, it is a generally accepted conclusion that the selection criteria of working fluids in different thermodynamic processes are quite different. This prompts us to think about how to apply the optimal working fluid to all thermodynamic processes at the same time in a thermodynamic cycle?

5. THE KNOWLEDGE GAPS AND DEVELOPMENT DIRECTIONS

From the above literature review, it could be found that the key thermophysical parameters affecting the cycle performance of traditional ORC were found out by using trail method and analytical method. However, a more unified quantitative expression of cycle performance and thermophysical parameters of working fluids needs to be clear, which could accurately reflect the degree of influence of different properties. Furthermore, it could be attempted to find parameters at the molecular level that affect key thermophysical properties of working fluid, which will be of great significance to the selection and design of working fluids.

Using decoupling method, more researches are needed to clarify the selection criteria for each thermodynamic process. The same research is also necessary for other thermodynamic cycles, such as heat pump cycles, absorption refrigeration cycles, etc. What's more, with the change of research roadmap, the development of the new generation of thermodynamic cycle is no longer follows the pattern of working fluid selection based on the cycle structure, but follows the pattern of cycle structure design based on working fluids. Working fluid should be considered as a new thermodynamic dimension in the construction of thermodynamic cycle. A 3D construction method of thermodynamic cycle was proposed in reference [29], which provides a feasible route to construct a novel thermodynamic cycle.

6. CONCLUSIONS

The researches on working fluid selection of organic Rankine cycle were comprehensive reviewed and classified according the research method, that is trial method, analytical method and decoupling method. For traditional ORC, the optimal working fluid could be selected depends on critical temperature, acentric factor, latent heat, liquid specific heat, Jacob number and the slope of working fluid saturated line in temperature-entropy diagram. Based on the review of working fluid selection, the congenital defects of traditional research could be found and the suggestions of research roadmap for efficient thermodynamic cycles is given.

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