Comparative analysis of properties of working fluids of power installations based on extended thermodynamic similarity

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Abstract. The influence of the thermophysical properties of the working fluid on the efficiency of the working cycle is considered. Using methods of thermodynamic similarity, it is shown that one of the important factors affecting the efficiency of the thermodynamic cycle is the ratio between the slope of the saturated vapor line in the entropy–temperature diagram and the slope of vapor isobars. The influence of the composition of the working fluid and the ability to control it for maximum efficiency is discussed.

1. Introduction

One of the urgent solutions for the efficient use of energy is the use of plants with the organic Rankine cycle (ORC) for the utilization of low-grade waste heat. Such systems are currently being developed for energy, transport and other systems [1, 2]. Relatively low-temperature boiling substances and sometimes mixtures are used as the working fluids of the ORC plants. Quite a lot of different requirements are imposed on working fluids, both in terms of thermophysical properties and technological features associated with the design of the plant, resource, safety, and minimal environmental impact. Therefore, the range of possible substances for use in a particular area is very limited. Sometimes it is practically impossible to choose a working fluid from among well-known substances in order to satisfy the requirements for safe operation of the installation. Therefore, the challenge remains to create new compounds and their compositions for ORC plants, in particular, for their use in transport and in other areas associated with increased operational requirements. It can be said that the situation is similar to that for refrigerants.

The peculiarity of low-grade energy sources is the temperature, which is insufficient for the operation of water steam power cycles. Low-grade energy sources include those sources whose temperature is about 400 °C.

When choosing a working fluid, it is necessary to proceed from the maximum efficiency of its use for a specific temperature range. In addition to efficiency, the size of a power plant is the most important economic factor. It happens that due to excessive sizes, the design of a power plant is impractical.

In the present paper, we consider the influence of the thermophysical properties of the working fluid on the efficiency of the working cycle of the installation, as well as on its possible weight and size characteristics (first of all, the sizes of the heat exchangers). To clarify the effect of various
thermophysical parameters, the relationships are analyzed that determine the specified characteristics of the installation of a given power, as well as their relationship. For generalization, the methods of extended thermodynamic similarity [3] are used, which make it possible in general to determine significant factors taking into account the nature (molecular features) of the working fluid. The possibilities of applying this approach for mixtures are also considered [4]. The developed technique [5] based on high-accuracy equations of state [6] allows to evaluate the accuracy of simpler methods based on equations of state with simple mixing rules.

The analysis was carried out in a general form, as well as for a number of specific working fluids having close boiling points (at normal pressure). As the calculations showed, the thermodynamic efficiency of the considered cycles relatively weakly depends on the type of working fluid at close values of the temperatures of heat supply and removal.

We suppose that the efficiency of a power plant is affected by the thermodynamic properties associated with the slope of the saturated steam and isobar lines in S–T coordinates (S is entropy, T is temperature), as well as the heat capacities of vapor and liquid phases. The properties of saturated liquid determine the work of the pump.

2. The influence of thermodynamic properties of the working fluid

The configuration of the cycle and the type of working fluid are closely related and affect the design of the main elements of the system. Currently, saturated and superheated steam cycles are generally used. A slight superheating of the steam is necessary to avoid erosion of the blades.

The slope of the saturated vapor line in S–T coordinates

\[ \zeta = dS / dT \]  

is one of the parameters that determine the features of the cycle.

Using thermodynamic relationships for pure substance one can write

\[ \frac{dS}{dT} = \frac{C_p''}{T} - \left( \frac{\partial V''}{\partial T} \right)_p \frac{dp}{dT} = \frac{C_p''}{T} - \left( \frac{\partial V''}{\partial T} \right)_p \frac{\Delta H_v}{T(V''-V')} \]  

where \( C_p'' \) is the isobaric heat capacity of saturated vapor, \( V'' \) is the volume of the saturated vapor, \( V' \) is the volume of the saturated liquid, \( \Delta H_v \) is the heat of vaporization.

As \( V'' \gg V' \), then the approximation \( (V''-V') \approx V'' \) is appropriate for the Equation (2).

According to the slope \( \zeta \), the working substances are classified as “wet” (\( \zeta < 0 \)), “dry” (\( \zeta > 0 \)) and “adiabatic” (\( \zeta = 0 \)) [7]. A typical cycles are shown in Figure 1. In some cases [8, 9], trans-critical cycles and cycles completely located in the supercritical region are used (Figure 2). When using mixed working fluids, isobaric processes of evaporation and condensation are accompanied by a change in temperature (Figure 3).

Figure 1. Organic Rankine cycles with “wet” (a) and “dry” (b) working fluids
Figure 2. Trans-critical (1–2–3–4–1) and super-critical (dashed lines) cycles

For the analysis of ORC, pure substances with close normal boiling points (~ 30 °C) were considered: methanol, pentane, hexane, methyl pentane, R11, R23, R113, R123, R141b, R152a. The properties of substances were taken from the NIST database [10]. Cycles were considered at the same ratio of minimum and maximum temperatures

\[ \tau = \frac{T_3}{T_1}, \]  

where \( T_3 \) is the normal boiling point.

Thus, the lower pressure is normal pressure. The temperature ratio was taken \( \tau = 0.5 \), which corresponds to the efficiency of the Carnot cycle \( \eta_c = 0.25 \).

Thermal efficiency of the theoretical cycle

\[ \eta = 1 - \frac{\Delta H_{2-3}}{\Delta H_{1-4}}, \]  

where \( \Delta H_{1-4} \) and \( \Delta H_{2-3} \) are corresponding changes in enthalpy.

The efficiency of the real cycle

\[ \eta_r = \frac{\Delta H_{1-2} \eta_t - \Delta H_{4-3} / \eta_p}{\Delta H_{1-4}}, \]  

where \( \eta_t \) is turbine efficiency, \( \eta_p \) is pump efficiency.

Since the pump is small, then \( \eta_r \approx \tau \eta_c \).

The calculations of the efficiency of the cycles for the above substances were performed using data on their thermodynamic properties [10].

An approximate analysis was also performed with no specific working fluid was considered. The parameters describing the working fluid were the isobaric heat capacity of saturated steam \( C_p \), the ratio of the heat capacities of saturated liquid and steam \( k_c = C_p^l / C_p^s \), and the heat of vaporization at normal boiling point \( \Delta H_v \). When using dimensionless expressions for the corresponding enthalpies in the framework of such an analysis, it was shown that, for a given \( k_c \), the cycle efficiency depends on the dimensionless quantity

\[ x = \frac{\xi}{\xi_p}, \]  

where

\[ \xi_p = (\partial S / \partial T)_p = C_p^s / T \]
is the slope of the isobar of steam near the saturation line. The quantity \( x \) is related to the specific heat by the relation

\[
x = 1 - \frac{K_{Tr}}{C_p''}
\]

(8)

where \( K_{Tr} \) is Trouton’s constant.

Figure 4 shows the dependences of the thermal efficiency on the parameter \( x \) and the isobaric heat capacity of the steam \( C_{p''} \). Solid lines show analytical estimates. Points are obtained as a result of calculations using tabulated data. The non-smooth conjugation of the dependences for \( \xi < 0 \) and \( \xi > 0 \) in Figure 4 is due to the fact that in the corresponding cycles the isobar heat supply and removal processes are different. For \( \xi = 0 \), these dependences coincide. Figure 5 illustrates the work of the pump.

**Figure 4.** Dependences of thermal efficiency on parameter \( x \) (a) and isobaric heat capacity of saturated vapor (b). Points correspond to calculation for substances: 1 – R21, 2 – R152a, 3 – R11, 4 – R141b, 5 – R123, 6 – R113, 7 – pentane, 8 – methyl pentane, 9 – methanol, 10 – hexane

**Figure 5.** The ratio of the pump work to the turbine (expansion device) work; (a), (b), 1–10 – see figure 4

The lines obtained as analytical estimates correspond to the efficiency values calculated from the tabular data. These differences are associated with differences in the Trouton constant and the ratio of the heat capacities of the liquid and vapor for various substances. For analytical estimates, these values were assumed constant and the same for all substances. We can say that analytical estimates demonstrate a qualitatively correct tendency to change the cycle efficiency depending on the
parameter $x$. Moreover, for the parameter $x$ this tendency is traced better than for the dependence of the efficiency on the dimensionless heat capacity.

It is known that “adiabatic” working fluids ($\xi = 0$) make it possible to realize the highest efficiency. Our study showed that the range of working fluids, for which the efficiency will be slightly lower, meets the criterion $|x| < 0.5$.

3. Modeling the properties of mixtures

For the analysis of mixed working fluids, it is necessary to consider the boundaries of the two-phase region. The construction of phase envelopes of mixtures is very important in phase equilibrium calculations with many applications. It is very useful for process simulation for the study of hydrocarbon fluids. The number of solutions for a given specification in calculation of saturation points is not known in advance. Furthermore, there may be multiple solutions or no solution at all. So the stepwise construction of the entire phase boundary was recommended to locate all solutions to a given set of specification [11, 12].

Phase equilibrium calculation with the specified vapor fraction $\beta$ and either the specified pressure or temperature is of considerable interest in industrial applications. The most important cases are bubble point calculations ($\beta = 0$) and dew point calculations ($\beta = 1$). The most reliable approach for locating all solutions to a given set of specifications may be the stepwise construction of the entire phase boundary [11]. The overall mixture composition and the vapor fraction, which can equal any value between 0 and 1, are specified in constructing phase boundary. We use the method of constructing phase boundary based on [12]. Constructing the phase envelope is started using a specification for which reasonable initial estimates can be generated and convergence is easily obtained. A low pressure is usually selected as a starting specification. After an initial point has been generated, subsequent phase envelope points are calculated using a Newton–Raphson method with initial estimates obtained from the previous point.

The analysis based on the high-precision equation of state GERG-2008 [6] showed that in the region not close to the critical point, the Peng–Robinson equation of state has good accuracy. As a test task for the developed algorithm based on the Peng–Robinson equation of state the calculations of the phase envelope has been performed for the methane–ethane mixtures. Results are compared with NIST database [10] and showed in Figure 6.

![Figure 6. Vapour–liquid phase envelopes of methane–ethane mixtures with molar fractions of methane 15%, 50% and 85%](image-url)
Figure 6 shows that the phase envelope calculated with the Peng–Robinson equation mostly coincides with NIST data, but in the vicinity of the critical point it doesn’t work well. In addition, Figure 6 also shows that with the molar fraction of ethane increasing, the phase envelope of the methane–ethane mixture moves to that of the pure ethane.

4. Conclusions
It is practically difficult to make a choice of acceptable working fluid so as to correspond to the required temperature range. Changing the boiling point is possible by adding a small fraction of another substance. The controlled composition of the mixed working fluid potentially allows to change the parameters of the cycle depending on changes in the operating conditions of the power plant. The presence of a temperature glide, as is known, can also increase the efficiency of heat transfer. In addition, the use of the mixture makes it possible to bring the properties of the working medium closer to the case of the “adiabatic” working fluid.

The most critical element of the ORC installation is the condenser, since in the process of heat removal during condensation the temperature difference between the working fluid and the environment is limited to the last value.

The analysis showed that the efficiency of systems with a “dry” working fluid is, as a rule, somewhat lower than that of systems with a “wet” working fluid. This is due to the loss of exergy on cooling superheated steam. Accordingly, it also increases the size of the heat exchanger. On the other hand, such a cycle allows the use of heat recuperation, but its feasibility is not obvious from an economic point of view. In general, it is not worth saying that a “dry” working fluid is less preferable, since the differences in efficiency are not so great.

The similarity criterion considered makes it possible to compare potential efficiency for the case of one working fluid with respect to the case of another, without performing detailed calculations. Due to the fact that recently created new working fluid, the possibility of such an assessment seems useful.

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