Molecular Complexity of Working Fluids Dedicated to Organic Rankine Cycle (ORC)

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Abstract. Organic Rankine Cycle (ORC) power plants are the most well-known and mature technology used to converting low and medium-temperature heat into electricity, especially from waste heat and renewable energy sources (including geothermal and solar thermal). Despite the level of development of ORC systems available on the market, there are still many aspects in the context of improving those units – constructing economically profitable low power unit, improving efficiency, selection an appropriate working fluid, etc. This paper analyzes 17 workings fluids dedicated to ORC system and discusses an existence of low stability region in their dense vapors and its influence on some peculiarities in behaviors of selected isentropic and dry fluids. The analysis shows relation between the retrograde phenomena in the flow of ORC fluids and mechanical and thermodynamic stability parameters.

1. Introduction

In opposition to fossil fuel, heat from waste or renewable resources is mostly available from low to medium temperature (in the range from 70 to 350 °C) [1]. The use of Organic Rankine Cycles (ORCs) allows for exploitation of heat that would be wasted in other cases. The working principle of Organic Rankine Cycle (ORC) power plant is common to the most widely used process for power generation – the Clausius-Rankine Cycle. The main difference between those two cycles is the use of organic working fluid in ORC instead of water (steam), which is used in conventional Clausius-Rankine Cycle. The use of organic substances with a lower boiling point and a higher vapor pressure instead of water allows to utilized low and medium temperature heat sources to produce electricity. The choice of working fluid is one of the most crucial things in designing ORC system – there is a lot of research [2-4], which discuss working fluid selection for ORC power plant. Authors agree that an organic working fluid selected to ORC should be fitted to heat source and its thermodynamic properties, thanks to that higher efficiencies of both cycle and expander can be obtained [5,6].

Maizza and Maizza [7] showed that there are other important features in working fluid selection for ORC such as: low toxicity, good compatibility and chemical stability in operation with other materials, low flammability, corrosivity and small potential for decomposition. Within the last years, many novel working fluids have been introduced, such as hydrofluoroolefines (HFO). A new generation of working fluids meet the criteria of environmental friendliness and are characterized by significantly smaller Global Warming Potential (GWP) compared to the currently widely used refrigerants [8]. Also, it can be observed an increase of siloxanes based on Organic Rankine Cycles across the Europe. They are increasingly chosen because of their advantages, such as: long-lasting, inflammable and more stable than carbo-organic fluids [9].
Lukawski, Tester and DiPippo [10] in their work analyzed impact of molecular structure of working fluids on Organic Rankine Cycle plant efficiency. They showed that maximum utilization efficiency of ORC system and the temperature of heat source can be predicted by using two parameters: the reduced ideal gas capacity and the critical temperature of working fluid. Works [11] and [12] analyzed an influence of molecular complexity and low-stability region on dense gas flows in ORC fluids.

Evaluation of Using Gas Turbine to Increase Efficiency of the Organic Rankine Cycle was obtained by Matuszewska and Oleczak [13].

2. Characteristic of ORC fluids

The organic fluids dedicated to ORC system can be used at much lower evaporation temperature than in water-steam Clausius-Rankine Cycle, what is also important – their superheating is not required. In order to generate mechanical power, organic fluids are expanded in turbine or expander. The dynamic of expansion strongly depends on the process conditions including the initial thermodynamic state and expansion ratio [11]. The working fluid selection is driven by different requirements and is strongly related to specific ORC application (temperature of heat source, compatibility, flammability and toxicity, the environment friendliness). Mostly ORC fluids can be characterized by belonging to organic chemical groups, high molecular weight, much lower temperature and pressure than water and the slope shape, which cause that the superheating of them is not required. These factors determinate that those working fluid can be used to the utilization of low and medium temperature heat. However, there are still some problems during ORC fluids selection, among others: an incomplete data in its thermal properties, problems with drop-in replacement of old generation and environmental harmful fluids.

On purpose of this paper, 17 working fluids have been chosen, table 1. The fluids have been arranged according to their chemical groups. In table 1, are listed representative of the formerly widely used fluids such as hydrocarbons (HC’s) and their derivatives (HFC, HCFC). Nowadays, they use of theme is taken under limitation due to their harmful impact on global warming and ozone depletion (high GWP and ODP). Also, representatives of new generation organic fluids have been taken under consideration – hydrofluorolefins (HFOs) dedicated to low temperature ORC plant and siloxanes – to medium temperature ORC systems.

| Table 1. Working fluids dedicated to ORC systems and their selected properties |
|-----------------------------|-----------------|-------------|-------------|-----------------|-----------------|
| Group                      | Name            | Mass molar M [g/mol] | Pc [bar] | Tc [K] | NBP [K] | Acentric Factor \( \varphi \) |
| Hydrocarbons (HCs)         | R600            | 58.12         | 37.9      | 425.1 | 273.0 | 0.201 |
|                            | Toluene         | 92.14         | 41.3      | 591.8 | 383.8 | 0.266 |
|                            | n-dodecane      | 170.0         | 29.3      | 374.9 | 256.8 | 0.357 |
| Hydrofluorocarbons (HFCs)  | R134a           | 102.0         | 40.6      | 374.2 | 247.1 | 0.327 |
|                            | R227ea          | 170.0         | 29.3      | 374.9 | 256.8 | 0.357 |
|                            | R245fa          | 134.1         | 36.5      | 427.2 | 288.3 | 0.378 |
| Hydrofluoroolefins (HFOs)  | R1234yf         | 114.0         | 33.8      | 367.9 | 243.7 | 0.276 |
|                            | R1234zeE        | 114.0         | 36.4      | 382.5 | 254.2 | 0.313 |
|                            | R1234zeZ        | 114.0         | 35.3      | 423.3 | 282.9 | 0.327 |
| Hydrochlorofluorocarbons (HCFCs) | R123    | 152.9         | 36.6      | 456.8 | 301.0 | 0.282 |
| Siloxanes                  | MM             | 162.4         | 19.4      | 518.8 | 373.4 | 0.418 |
|                            | MDM            | 263.5         | 14.2      | 564.1 | 425.7 | 0.529 |
|                            | MD2M           | 310.7         | 12.3      | 599.4 | 467.5 | 0.668 |
|                            | MD4M           | 459.0         | 8.8       | 653.2 | 533.9 | 0.825 |
|                            | D4             | 296.6         | 13.3      | 586.5 | 448.5 | 0.592 |
|                            | D5             | 370.8         | 11.6      | 619.2 | 484.1 | 0.658 |
|                            | D6             | 444.9         | 9.6       | 645.8 | 518.1 | 0.736 |
The organic fluids from table 1 can be divided into two groups: the first one with high-boiling point (NBP) close to the ambient temperature (include siloxanes, n-dodecane and toluene), the second one with low-boiling point, which includes almost all hydrocarbons (and their derivatives). Table 1 shows also correlation between growth of acentric factor $\omega$ and rise of molecular mass of organic fluid.

2.1. The saturation vapor curve

Thanks to the shape of the saturation line, organic fluids can be divided into three groups: wet, isentropic and dry. The shape of the saturation line is one of the most important aspects characteristic ORC plant – it is taken under consideration during system designing and equipment selection – because it influences system efficiency. The figure 1 represents all three saturation vapor curve types: a negative slope for wet fluid (for water ammonia), nearly vertical vapor saturation curve for isentropic fluid (R11) and a positive slope for dry fluid.

![Figure 1. The saturated vapor curve for fluids (a) wet, (b) isentropic and (c) dry [3]](image)

Dry and isentropic fluids are best recommended for ORC plant – both do not need superheating, which eliminates concerns connected with turbine blades corrosion. From these two, the isentropic fluid is more recommended – because there is no need to use regenerator in such system and the saturated vapor at the turbine inlet expands along vertical line and remain saturated leaving the turbine.

2.2. ORC fluids behavior on saturated line

Recent research focuses on the influence of organic fluids molecular characteristics and dense-gas flow phenomena, which is not well known nowadays. Heavy organic fluids dedicated to ORC systems have composed molecular structure which causes that they do not behave classical near the saturated vapor curve ($x=1$). In this light, it seems very important to study and analyze the measures of fluid complexity and associated theme with fluid behaviour and parameters.

From the molecular complexity, the shape of slope of saturation vapor curve can be predicted. Thereby, the information whether fluid is wet, isentropic or dry can be given. For this purpose, coefficient $\sigma$ can be used – this factor is usually referred to the reduced temperature $T_r = 0.7$ and it defined by equation 1:

$$
\sigma_{T_r=0.7} = \frac{T_c}{R} \left( \frac{d\psi}{dT} \right)_{x=1} = \frac{T_c}{R} \left[ \frac{\partial \psi}{\partial \theta} \left( \frac{dp}{dT} \right)_{x=1} + \frac{\partial \psi}{\partial T} \right]_{T_r=0.7}
$$

Equation 1 can be presented in simplify form:

$$
\sigma_{T_r=0.7} = \frac{T_c}{R} \left( \frac{\partial \psi}{\partial \theta} \left( \frac{dp}{dT} \right)_{x=1} \right)_{T_r=0.7}
$$

The $\sigma$ coefficient is a heat capacity function and is directly related to the fluid molecular structure. When molecular complexity increase, the decrease of the heat capacity ratio $\gamma$, can be observed. It tends the slope of the saturation vapor curve become positive – the more positive slope is, then the more complex molecular structure can be observed (figure 2):
The ‘retrogradicity’ parameter proposed by Lambrakis can be used as counterpart formulation [14]:

$$ r_p = \frac{\partial T}{\partial p} \left( \frac{\partial s}{\partial p} \right)_{T=1} \geq 0 $$

(3)

This parameter is a very useful tool during supercritical and high-pressure subcritical ORC cycle analysis to shows difference from normal fluid behaviour. Because this case considered as real-gas expansion in the expander, temperature and pressure deeply influence variation of all physical constants. Eq. 3 can be written in form:

$$ r_p = \left( \frac{\tau_T}{\tau_p} \right) \left( \frac{\tau_v}{\tau_T} \right) \left( \frac{1 - \nu'}{\nu^v} \right) - 1 \geq 0 $$

(4)

Where parameters $\tau_{Tv}$ and $\tau_{vT}$ are two Virial Compressibility Derivatives (VCD) functions [15,19]. The use of Maxwell thermodynamic relations and the Legendre transformation can help to obtain VCD’s:

$$ \tau_{Tv} = z + T \left( \frac{\partial z}{\partial T} \right)_T = z + T \left( \frac{\partial z}{\partial T} \right)_v $$

(5)

$$ \tau_{vT} = z - v \left( \frac{\partial z}{\partial v} \right)_T = z - v \left( \frac{\partial z}{\partial v} \right)_v $$

The reduced form can be written:

$$ D = \left( \frac{\nu'_T}{\nu'_v} \right) $$

(6)

With some changes, it can be presented as:

$$ D = - \left( \frac{\partial v}{\partial s} \right)_T \left( \frac{\partial T}{\partial s} \right)_p = - \frac{T}{c_p} \left( \frac{\partial p}{\partial v} \right)_T $$

(7)

The reduced form can be written:

$$ D = D \left( \frac{\nu'_v}{\nu'_T} \right)^2 = \frac{R}{\nu'_v} \frac{\tau'_v}{\tau'_T} $$

(8)

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**Figure 2.** Wet, isentropic and dry fluids [12]
This equation can be used to analyze the stability criterion for ORC fluids in their dense vapor region on the saturation curve. Figure 3 presents examination of stability criterion for R245fa. Some peculiarities in behaviour of isentropic and dry ORC fluid, have been shown during observation. A low stability of dense gas in the high-pressure region of slightly superheated vapor can be noticed. From figure 3 can be concluded that the reduce stability D of R245fa dense vapor shows in region with the temperature range $438 < T_r < 445$ K and pressure $0.85 < p_r < 1.3$. The local minima and saddle points of isoclines of constant D can be reveal around the saturated vapor state.

![Figure 3. Reduce thermodynamic stability D of R245fa](image1)

The characteristic gas parameter is its isentropic index $k_s$, which shows the relation below:

$$k_s = \left( \frac{\gamma}{\gamma - 1} \right) \left( \frac{p}{p_i} \right)^{\gamma - 1}$$

(9)

Figure 4 shows an example of the relationship of the isentropic index as a function of reduced pressure and temperature for R245fa:

![Figure 4. Isentropic index for R245fa](image2)

Figure 4 clearly shows that the isentropic index ceases to be sensitive to pressure changes as the temperature increase. Its largest fluctuations are observed near the saturation curve, and its value is inversely proportional to the pressure increase.

Reduced thermodynamic stability criterion D on the saturated vapor line (x=1)
for all selected working fluids has been shown on figure 5. The working fluid arrangement is based on the acentric factor \( \omega \). This listing has been made for three important points on the saturated vapor curve: including temperature corresponded to \( s'' = \text{max} \) and \( h'' = \text{max} \) and reduced temperature \( Tr=0.7 \).

![Figure 5. Stability criterion D vs acentric factor \( \omega \) for ORC fluids](image)

Analyzing fig. 5, it can be noticed that the stability criterion D on the saturation line for reduced temperature \( Tr=0.7 \) achieved values close to zero for high molecular mass and complex fluids (siloxanes). The stability criterion (for reduced temperature \( Tr=0.7 \)) for hydrocarbons and its derivatives is minimally higher and positive. Almost linear dependence to the Pitzer’s criterion \( \omega \) obtain the stability criterion D for temperature corresponding to \( h'' \text{max} \). There is hard to observe any regularity to the \( \omega \) for \( s'' \text{max} \) data. The stability criterion D is almost the same for both \( h'' \text{max} \) and \( s'' \text{max} \) conditions on the saturated vapor line for siloxanes. Also, for all considered ORC fluids, the stability criterion D for temperature corresponding to \( s'' \text{max} \) is lower to those with \( h'' \text{max} \).

3. Conclusions

The analysis shown in this paper confirms that some peculiarities appear in high dense gas region of ORC fluids. They are corresponding to the thermodynamic parameters and compressible flow conditions. For high -molecular mass and complex fluids such as siloxanes, it has been observed that the stability criterion D on the vapor-liquid line is nearly zero. Higher and positive value of stability criterion (\( D = 0.14\pm0.23\cdot10^{-3} \)) is obtained for butane, toluene, R123, R227ea, R245fa and the HFO group R1234ze. It is easy to observe nearly linear dependence of D respect to \( \omega \) factor for the conditions of enthalpy maxima \( h'' \text{max} \). However, the maxima of saturated vapor entropy \( s'' \text{max} \) for all investigated ORC fluids do not show any regular variation to the Pitzer’s criterion \( \omega \). It should be noticed that the \( s'' \text{max} \) maxima for all investigated ORC fluids corresponds to the lower reduced temperatures than values obtained for the \( h'' \text{max} \).

The working fluid selection for ORC cycles is hard and complex – a lot of factors and relationships occurred that should be always individually considered during designing process. The complexity of ORC fluids selection is hard to understand good enough due to the lack of thermodynamic data. The best working fluids for ORC are isentropic and dry ones but they should be chosen individually, depending on temperature of heat sources, environmental criteria and thermodynamic properties of ORC fluids. It is important to remember that all fluids dedicated to ORC systems have high-molecular complexity which influences their behavior. The use of complete real properties of ORC fluids can improve selection process by showing real performances and efficiency of ORC systems.
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