CRITERIA FOR SELECTION OF WORKING FLUID IN LOW-TEMPERATURE ORC

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The economics of an ORC system is strictly linked to thermodynamic properties of the working fluid. A bad choice of working fluid could lead to a less efficient and expensive plant/generation unit. Some selection criteria have been put forward by various authors, incorporating thermodynamic properties, provided in literature but these do not have a general character. In the paper a simple analysis has been carried out which resulted in development of thermodynamic criteria for selection of an appropriate working fluid for subcritical and supercritical cycles. The postulated criteria are expressed in terms of non-dimensional numbers, which are characteristic for different fluids. The efficiency of the cycle is in a close relation to these numbers. The criteria are suitable for initial fluid selection. Such criteria should be used with other ones related to environmental impact, economy, system size, etc. Examples of such criteria have been also presented which may be helpful in rating of heat exchangers, which takes into account both heat transfer and flow resistance of the working fluid.

Keywords: micro CHP, organic Rankine cycle

1. INTRODUCTION

In recent years there is a clear tendency, both worldwide and in the countries of European Union (EU), to increase the importance of the so called dispersed energy generation. That is based on the local energy sources and technologies utilizing both fossil fuels and renewable energy resources. Combined micro heat and power units (CHP) utilizing the organic Rankine cycle (ORC) fit very well to that strategy. In recent years that technology attracted intense research. It appears to be a promising technology for conversion of heat into useful work and electricity, especially in the light of the fact that the heat source in case of disperse systems can be of various origin, just to mention for example solar power, biomass combustion, geothermal heat or waste heat. Unlike in the steam power cycle, where vapour of water is the working fluid, ORC uses refrigerants, hydrocarbons, solvents or other organic substances. It is commonly acknowledged that below 350 °C the performance of ORC cycle is better than that of a traditional steam Rankine cycle.

Generation of electricity on a small domestic scale together with production of heat can be obtained through employing gas engine units, micro gas turbines, fuel cells with efficient electrolysis, Stirling engines or ORC systems. Some of the technologies are mature and have demonstrated their commercial performance, whereas others are at their earliest stages of market entry and are still relatively expensive. Another issue is that they may not perform to their expected potential. The ORC technology is currently quite popular, especially in case of 100 kWe to 1 MWe generated power. Is case of smaller,
domestic installations (1-5 kWe) these technologies are still immature, primarily due to the commissioning issues of prototype installations and excessive unit costs, but they are likely to become significantly cheaper over the next few years as the installations enter the mass production. In our opinion the ORC technology is likely to be fully mature much earlier than other promising technologies such as Stirling engines and fuel cells, as the components for micro ORC are already commercially available and a lot of research has been accomplished into development of respective cycle elements. With the advent of these technologies the electrical efficiency levels, currently at around 10% mark, are likely to rise to reach 25%. Authors own unpublished yet studies show that the level of efficiency of 40% is also possible.

The up to date research into small scale CHP was focused mainly on subcritical cycles. There is, however, also an unexplored area of supercritical parameters which could also be analysed. Supercritical fluid parameters are much easier to be realized than those for water. However, there is some limitation in case of domestic micro CHPs. The challenging objective for a domestic micro CHP is also to design small size heat exchangers and for that reason not all supercritical fluids could be suitable. It is well known that the heat transfer to gases is much less efficient than that to two-phase fluids and that leads to excessive sizes of heat exchangers. However, in cases where the volume of heat exchangers is not an issue supercritical cycles may prove to be a viable option.

In the paper, apart from presentation of existing methods of selection of working fluids a simple analysis has been carried out which resulted in development of a thermodynamic criterion for selection of an appropriate working fluid. The postulated criterion is related to non-dimensional numbers, which are characteristic for different fluids. The efficiency of the cycle is in a close relation to these numbers. The criterion is suitable for initial fluid selection. Such criterion should be used with other criteria related to environmental impact, as mentioned in the following section. Additionally, another criterion is postulated which may be helpful in rating of heat exchangers, which takes into account both heat transfer and flow resistance of the working fluid. The criteria developed have a much wider application and can be used for other temperature ranges also boiling point liquid.

2. SELECTION OF APPROPRIATE WORKING FLUID FOR ORC INSTALLATION

Selection of working fluid is an important aspect of attaining possibly high cycle efficiencies. That enables optimal utilization of available energy sources. There is a wide selection of organic fluids, which can be used in ORC systems. Maizza and Maizza (2001) conducted investigations with different organic fluids for systems with heat recovery. The most important features of a good organic working fluid are:

- low toxicity,
- good compatibility and chemical stability in operation with other materials,
- low flammability, corrosivity and small potential for decomposition.

An important aspect for the choice of the working fluid is the temperature of the available heat source, which can range from low temperatures of about 70 °C to temperatures of about 350 °C. According to many authors above 350 °C water is better as the working fluid than organic fluids. At low temperatures organic fluids lead to higher cycle efficiency than water. Additionally, the wet steam causes operational problems. Refrigerants are thought to be the most promising fluids for ORC cycles, especially in view of their low toxicity.

Following our experience the simplest configuration of Rankine cycle was assumed for realization of domestic ORC (Mago et al., 2008). The simplicity of the cycle is believed to result in possibly small heat transfer surfaces of heat exchangers, which are a decisive factor in final dimensions of the micro CHP for domestic use. There is an abundant literature concerning fluids for that purpose, but these
primarily relate to low or medium enthalpy heat sources: Andersen et al. (2005), Drescher & Bruggemann (2007), Liu et al (2004), Mikielewicz & Mikielewicz (2008 and 2009), Nowak et al. (2008), Saleh et al. (2007), Saleh et al. (2009), Tchanche et al. (2009), Wei et al. (2007). The fluids which were considered in the present study have been carefully selected from amongst 24 others considered from the Refprop 10 database (2010).

Recently many other studies showed the selection of working fluids was very important for the ORC system performance, see for example Bao and Zhao (2014), Cho et al. (2014) or Garg et al (2013). Rayegan et al. (2011) who developed a procedure to compare the thermodynamic properties of working fluids under similar working conditions. Aljundi et al. (2011) analyzed the effects of using alternative dry fluids on the efficiency of the ORC and compared them with other refrigerants. Recently, research work by Aghahosseini and Dincer (2013), focused on analysing multi-component mixtures of working fluids in order to better match the heat and cold sources.

Our analysis focused only on pure fluids. Pure working fluids can produce binary mixture combinations. Their features are out of the scope of present paper.

Fluids applicable to ORC are featuring in general three possibilities of the slope of saturated vapour line, namely a positive slope of saturated vapour line (SES 36, HFE7000), a negative slope (ethanol, R134a, water, ammonia) and almost isentropic distribution of temperature versus entropy (R141b, R245fa), Fig. 1. That has a bearing on the course of expansion line meaning that the expansion process in the first case is all the way through the superheated steam region, in the second one in the wet steam region whereas in the third one partially in the wet region and finally terminating just in the superheated steam region. Dry and isentropic fluids exhibit better thermodynamical efficiencies of expansion devices, as there is no condensation in the turbine expansion, contrary to wet fluids. On the other hand such fluids require larger heat transfer surfaces. In many cases a regenerator is usually used. The dry fluids used in Maizza and Maizza (2001) investigations were R113, R123, R245ca and isobutene. Refrigerant R123 has been dedicated to be the best fluid.

Fig. 1. Comparison of different working fluids: a) expansion proceeds along the vertical and isentropic saturated vapour line (isentropic fluid), b) „wet” and c) „dry”

It is apparent that heat transfer to vapour exhibits smaller values than in the case of wet vapour and therefore has an influence on the size of equipment. Small dimensions (volume) of heat exchangers (condenser and evaporator channels) require also analysis of pressure drops in these exchangers, which influence cycle parameters and, as a consequence, temperature differences in heat exchangers and also the exchanger dimensions.

Up to date research was focused mainly on subcritical cycles. There is, however, an unexplored area of supercritical parameters which offer also great opportunities for exploitation. The analysis of
Supercritical fluid parameters may lead to higher efficiencies rendering the micro CHP even more attractive. The critical point of organic fluids is reached at lower pressures and temperatures compared with steam. Therefore supercritical fluid parameters are much easier to be realized in practical applications. Small volume of heat exchangers is crucial for domestic micro CHP and for that reason not all supercritical fluids are suitable.

Typically, the algorithm of calculations is based on well-known relations describing the Rankine cycle. Normally it is assumed that the maximum pressure in domestic installation should not exceed 60 bar nor temperature of intermediate heating oil 300 °C, respectively. Notation of state points for subcritical and supercritical cycles is presented in Fig. 2.

Summarising a good working fluid for thermodynamic ORC cycles should feature Mikielewicz and Mikielewicz (2008, 2009):

- small specific volume after expansion in a turbine,
- low viscosity and surface tension,
- high thermal conductivity,
- adequate thermal stability,
- low corrosion potential,
- cannot be toxic, but compatible with other materials and lubricants,
- additionally, the vertical vapour saturation curve is welcome, as on one side a low moisture content of vapour influences expansion (small erosion of turbine blades), and on the other hand in the condenser there is no removal of heat from the superheated vapour but straight away vapour condensation proceeds,
- advantageous will be fluid, which in the condenser will have a pressure higher than atmospheric, which will prevent air penetration into the system.

In a concept of the micro heat and power plant which would be used for production of electricity and heat in households, the heat transfer would take place in a boiler and condenser.

The sub-critical ORCs are different types according to the shape of the saturated vapour curve in the temperature versus entropy diagram. As mentioned earlier, we distinguish two types of ORC processes with the negative or positive slope of the saturated vapour curve in the T–s diagram, as shown in Fig. 1. As shown in Figs. 1 and 2, the working fluid leaves the condenser as saturated liquid (state point 3). Then, it is compressed by the liquid pump to the sub-critical pressure (state point 4). The working fluid is then heated in the evaporator until it becomes saturated vapour (state point 1). The saturated vapour flows into the turbine and is expanded to the condensing pressure (state point 2). At the condensing pressure, the working fluid lies in the wet (Fig. 1b) or superheated vapour region (Fig. 1c). The vapour passes through the condenser where heat is removed until it becomes a saturated and subsequently
saturated liquid (state point 3). In the cycle, as described in Fig. 1c, if the temperature \( t_2 \) is markedly higher than the temperature \( t_4 \), it is strongly advised to implement the internal heat exchanger (IHE) into the cycle. In such case the turbine exhaust flows into the internal heat exchanger and cools in the heat exchanger in the process (2–3) by transferring heat to the compressed liquid that is heated in the process (5–6), Fig. 4. Next, an isentropic vapour saturation line is desirable as on one hand it prevents the turbine blades from erosion and on the other hand the superheated vapour is not required to be cooled in the condenser and only pure condensation (phase change) process is required. Another feature of the working fluid is the requirement that the fluid has a higher pressure than atmospheric in condenser, which prevents the air from penetrating to condenser.

![Fig. 3. ORC with negative slope of saturated vapour curve](image1)
![Fig. 4. ORC with positive slope of saturated vapour curve](image2)

In a large industrial installation the cost of working fluid is a very important element and hence it attracts so much attention. In some cases it can be proved that the less efficient thermodynamically working fluid is more cost efficient as it turns out to be cheaper in the overall economic balance of the system. Majority of modern fluids suitable for use in ORC installations are rather expensive. Scarcely they are organic or natural. The criterion suggested in the paper is merely the preliminary indicator for initial selection. At the final selection other criteria must be also employed such as for example economic or toxicity criteria.

Theoretically every fluid could be used as working fluid in the thermodynamic cycle, if only it is used in the appropriate temperature range. In practice there can be several characteristic features of the potential working fluid to be selected for use in the particular cycle. The selection of the working fluid is an important element of attaining the highest possible cycle efficiencies, which on the other hand allows for optimal utilization of available energy sources. Presented below are some thermodynamic criteria for initial selection of the working fluid, for the case of subcritical cycle and supercritical cycle.

**2.1. Subcritical “wet” cycle**

The analysis of subcritical wet cycle commences with the expression for the cycle efficiency, Fig. 5:

\[
\eta = \frac{l_{\text{cycle}}}{q_m} = \frac{h_1 - h_5}{h_1 - h_3} \tag{1}
\]

Enthalpies present in Eq. (1) can be written in terms of a corresponding liquid saturation state, and the enthalpy prior the expansion can be written in terms of \( h_3 \):
Relation (3) is a general formula describing the state after expansion in the turbine. In case of dry fluids \( x_2 = 1 \) whereas in case of wet fluids \( \Delta h_{\text{superheat}} = 0 \). In general the two latter terms in Equation (3) can be combined to yield:

\[
h_2 = h_3 + \Delta H(T_2)
\]

Substituting all these information into (1) we obtain the cycle efficiency:

\[
\eta = \frac{\frac{h_3 + c_p(T_1 - T_2) + h_{l_1} - h_3 - \Delta H(T_2)}{h_3 + c_p(T_1 - T_2) + h_{l_1} - h_3}}{\frac{\Delta H(T_2)}{c_p(T_1 - T_2) + h_{l_1}}} = 1 - \frac{\Delta H(T_2)}{c_p(T_1 - T_2) + h_{l_1}}
\]

Temperature difference between condensation and evaporation levels can be expressed in terms of Carnot cycle efficiency and then for the subcritical cycle:

\[
\eta = 1 - \frac{\Delta H(T_2)}{h_c(T_i)} = 1 - \frac{\Delta H(T_2)}{h_c(T_i) \eta_c + 1}
\]

Analysis of Equation (6) enables to conclude that the overall cycle efficiency is a function of a ratio \( \Delta H(T_2) / h_{v_1} \) and the Jakob number. It stems directly from Eq. (6) that we should consider the ratios of \( \Delta H(T_2) / h_{v_1} \) and \( c_p / h_{v_1} \) when we want to consider a substance as a working fluid. In other words it is not only that the fluid should feature a high value of specific heat and a low value of latent heat of evaporation, but the ratio of these values should assume high values for specified values of temperatures of upper and lower heat sources. Authors in general advise to use mean values of specific heat in the required temperature range; alternatively the mean specific heat can be obtained as a ratio of the difference of enthalpies to temperature difference. Similar analysis can be performed for the nominator in Eq. (6) from which it results that the ratio \( \Delta H(T_2) / h_{v_1} \) should assume the smallest possible values in order to attain high values of overall efficiency.

### 2.2. Subcritical “dry” cycle

Similar considerations lead to proposing a relevant working fluid for a cogenerative power plant with dry organic fluid as working fluid without superheating. For the case of a dry fluid and the presence of regenerator heat exchanger we obtain a smaller demand for external heat in the evaporator.

In case of dry fluid the internal regeneration should also be considered, Fig. 5. All modifications of the ORC’s improving their efficiency lead to additional heat exchanging areas and small improvements of effective efficiency.

In the analysis of dry fluid the following assumptions were made:

- external heating of liquid phase of working fluid takes place from temperature \( T_R \),
- temperature \( T_R \) corresponds to state 2, which can be found on interception of isentrope \( s_1 \) and isobar corresponding to condenser pressure, \( p_{\text{sat}}(T_c) \)
- working fluid properties are constant in the entire thermodynamic cycle,
- pump work, pressure drop in HE and expansion irreversibilities in turbine are neglected
- efficiency of regenerator is assumed as 100%.
The major difference in definition of the cycle efficiency is that contrary to the cycle without regeneration the heat supplied to the cycle is equal to enthalpy difference between states 6 and 1, instead of 5 and 1. Therefore it yields:

$$\eta = \frac{w_f}{\dot{q}_k} = \frac{h_1 - h_2}{h_1 - h_0} = 1 - \frac{\frac{h_{v_i}(T)}{c_p(T_p - T_R)} + h_{v_s}(T_p)}{T_s\bar{c}_{ps}}$$  \hspace{1cm} (7)

Cycle efficiency (7) can be now presented in the final form:

$$\eta = 1 - \frac{h_{v_i}(T_p)}{T_s\bar{c}_{ps}} - \frac{\bar{c}_{ps}}{\bar{c}_{pv}} \frac{T_p}{T_s} \frac{\frac{\bar{c}_{ps}}{\bar{c}_{pv}} \left( \frac{T_p}{T_s} \right)^{\bar{c}_{ps} - \bar{c}_{pv}} + h_{v_i}(T_p)}{\exp(k)}$$  \hspace{1cm} (8)

We can now introduce to Eq. (8) the appropriately defined Jakob numbers, defined on the basis of evaporation temperature of working fluid, temperature of its condensation and the Carnot efficiency. Consequently we get:

$$\eta = 1 - \frac{1}{Ja_i(T_p)}$$  \hspace{1cm} (9)

In Eq. (9) the Jakob number definitions are as follows:

$$Ja_i(T_p) = \frac{T_s\bar{c}_{ps}}{h_{v_i}(T_s)} \quad Ja_i(T_p) = \frac{T_s\bar{c}_{ps}}{h_{v_i}(T_p)}$$  \hspace{1cm} (10)

Analysis of expression (9) or the equivalent (10) allows for thermodynamic analysis of the cycles with regeneration and the selection of the working fluid with the view of its implementation in the ORC. The results obtained with the criterion are approximate, but it may be a very useful tool in the initial analysis of a large number of fluids with the view of their pre-screening. The criterion shows that in the case of so called dry fluids the regenerative heat recovery is not always possible. In such case the slenderness of the saturation curves is important which is expressed through the ratio of respective Jakob numbers $Ja_i(T_p)$ to $Ja_i(T_s)$. The second value is smaller than the first one and normally the ratio
assumes values greater than unity. The closer that ratio is to unity the better the efficiency of the cycle. The necessary condition for the regeneration is that $T_2 > T_5$. The thermodynamic analysis has been applied to the following fluids: ammonia, perfluorobutane C₅F₁₂, ethanol, heptane, isohexane, methanol, R11, R113, R123, R141b, R227, R245ca, R245ea, R365mfc, SES36, toluene and water. In subsequent studies the expansion of the list to further fluids is envisaged.

### 2.3. Supercritical cycle

In the selection of appropriate fluids at supercritical parameters, a simple analysis has been carried out which resulted in development of a criterion for selection of a good fluid. The analysis commences with the expression for the cycle efficiency (1). In relation (1) enthalpy change due to presence of the pump has been neglected. Enthalpies present in (1) can be written in terms of temperatures and fluid properties. Following some re-arrangements for the supercritical case of ORC a relation expressing the supercritical cycle efficiency can be obtained:

$$\eta = \frac{h_3 + c_p(T_1 - T_2) - h_3 - \Delta H(T_2)}{h_3 + c_p(T_1 - T_2) - h_3 - \Delta H(T_2)} = 1 - \frac{\Delta H(T_2)}{c_p(T_1 - T_2)}$$  \hspace{1cm} (11)

Temperature difference between condensation and evaporation levels can be expressed in terms of the Carnot cycle efficiency and then Eq. (11) after re-arrangement reads:

$$\eta = 1 - \frac{1}{c_pT_1}\frac{\Delta H(T_2)}{\eta_c} = 1 - \frac{1}{Ja(T_1, T_2)\eta_c}$$  \hspace{1cm} (12)

Analysis of Eq. (12) exhibits that efficiency of supercritical cycle depends on the modified Jacob number.

The thermal efficiency takes into account only the first law of thermodynamics (energy balance) without taking into account the qualitative difference between heat and work. In order to include into analysis limitations imposed by the second law of thermodynamics the exergy efficiency should be used. The exergy of thermodynamic system is defined as a potential maximum work that can be produced if the system is brought into equilibrium with its surroundings. The exergy of the fluid stream is given by the expression proposed by Bertrand et al. (2008), Braimakis et al. (2014):

$$E = \dot{m}\left[h - h_0\right] - T_0\left[s - s_0\right]$$  \hspace{1cm} (13)

In Eq. (13) the subscript 0 refers to the conditions of the ambient surroundings (usually in calculations $T = 15 \, ^{°}C$, $p = 1$bar). The exergy efficiency of the cycle is expressed as the ratio of the actual work produced by the cycle and amount of exergy of the heat source that flows into the system:

$$\eta_{ex} = \frac{W}{E}$$  \hspace{1cm} (14)

This efficiency reflects the heat source utilization and heat transfer between the working fluid and the heat source. Both the thermal and heat source utilization efficiency parameters are equally important for goodness of the cycle. However, the maximization of energy and exergy efficiency does not necessarily lead to optimized cost of the system, since it can involve excessively large heat exchangers or other equipment (e.g. turbine/piping, pomp) and consequently much higher capital costs.

Apart from the exergy efficiency some other parameters are equally important for choosing a good working fluid from the point of view of feasibility and economy. Such parameters are the rotational speed $n$ of the turbine, the size $SP$ of the turbine, the volume flow rate at the inlet and outlet from the
turbine and the UA value (overall heat transfer coefficient U multiplied by the heat transfer area A) for heat exchangers (evaporator, condenser and regenerator). Definitions of these parameters were presented by Bertrand et al. (2008), Braimakis et al. (2014):

\[ n = \frac{\Delta h_{\text{is}}^{0.75}}{10 \sqrt{V_{\text{exp}}}} \]  

(15)

Extremely high rotor speeds may be non-feasible or very expensive (including problems with proper bearings for the turbine shaft). \( SP \) and \( VFR \) are values associated with turbine size and technical complexity.

\[ SP = \frac{\sqrt{V_{\text{exp}}}}{\Delta h_{\text{is}}^{0.25}} \]  

(16)

\[ VFR = \frac{V_{\text{out}}}{V_{\text{in}}} \]  

(17)

\[ UA = \frac{\dot{Q}}{\Delta T_{\text{log}}} \]  

(18)

In the above equations \( \Delta h_{\text{is}} \) is the isentropic specific enthalpy drop in the turbine, \( V_{\text{exp,in}} \) and \( V_{\text{exp,out}} \) are the volume flow rates of the working fluid at the turbine inlet and outlet respectively, \( \dot{Q} \) is the rate of heat transferred in the heat exchanger and \( \Delta T_{\text{log}} \) is the logarithmic mean temperature difference between the heat transferring fluids.

3. RESULTS OF CALCULATIONS

Sample calculations for several fluids for the subcritical conditions have been presented in Table 1.

We can notice from there that the criterion is reflecting the ratio of \( \Delta H(T_2) / h_b(T_1) \) and \( c_p T_1 / h_b(T_1) \). In the case of a supercritical cycle the overall cycle efficiency is inversely proportional to the Jakob number, defined in a slightly different manner, i.e. \( Ja(T_1, T_2) = \frac{c_p T_1}{\Delta H(T_2)} \), for the determined Carnot efficiency. It stems directly from (6) that we should consider the \( c_p T_1 / \Delta H(T_2) \) ratio when we want to choose a substance as a working fluid. We would like that term to attain the highest possible values, i.e. the higher the value of Jakob number \( Ja(T_1, T_2) \) the higher the resulting thermal efficiency. Calculations for that case are presented in Table 2.

Table 1. Characteristics of cycle efficiencies for subcritical cycle parameters, Carnot efficiency \( \eta_c = 0.271 \).

| Fluid   | \( T_1 \) | \( P_1 \) | \( h_1 \) | \( h_2 \) | \( h_3 \) | \( h_4 \) | \( \eta_{\text{th}} \) Eq. (1) | \( \eta_{\text{b}} = \eta_{\text{th}} / \eta_c \) | \( Ja(T_1) \) | \( \Delta H(T_2)/h_{v1} \) | \( \eta_{\text{th}} \) Eq. (6) |
|---------|----------|----------|----------|----------|----------|----------|-----------------|-----------------|--------------|-----------------|----------------|
| R365mfc | 170.00   | 24.362   | 548.63   | 495.93   | 268.94   | 270.84   | 0.190           | 0.696           | 8.90         | 2.767          | 0.188          |
| heptane | 170.00   | 5.650    | 882.77   | 773.34   | 312.14   | 312.98   | 0.192           | 0.708           | 4.55         | 1.805          | 0.192          |
| pentane | 170.00   | 22.259   | 556.48   | 454.83   | 33.53    | 33.53    | 0.194           | 0.718           | 7.17         | 2.371          | 0.194          |
| R123    | 170.00   | 29.372   | 461.89   | 420.15   | 251.06   | 253.00   | 0.204           | 0.745           | 8.11         | 2.551          | 0.202          |
| R141b   | 170.00   | 25.061   | 540.98   | 481.18   | 257.83   | 259.77   | 0.213           | 0.780           | 4.95         | 1.847          | 0.211          |
| ethanol | 170.00   | 15.880   | 1373.1   | 1136.1   | 328.67   | 330.70   | 0.227           | 0.838           | 2.49         | 1.294          | 0.227          |
Advantage of the presented criterion lies in the possibility of selection of a working fluid without tedious calculations of thermal cycle efficiencies, through merely the knowledge of parameters constituting the Jakob number and $\Delta H(T_2) / h_v$ in case of supercritical cycle. The criterion points that the best one from those considered thus far is R141b and ethanol. Apart from the postulated thermodynamic criterion also other criteria should be considered such as influence on a human, environment, explosive character. The proposed criterion refers merely to high thermal efficiency.

Table 2. Characteristics of cycle efficiencies for supercritical cycle parameters, Carnot efficiency $\eta_c = 0.317$.

| Fluid   | $T_1$ | $P_1$ | $h_1$ | $h_2$ | $h_3$ | $h_4$ | $\eta_{th}$ Eq. (1) | $\eta_{th} = \eta_{th}/\eta_c$ | $Ja(T_1,T_2)$ | $\eta_{th}$ Eq. (9) |
|---------|-------|-------|-------|-------|-------|-------|---------------------|--------------------------|----------------|-------------------|
|         | °C    | bar   | kJ/kg | kJ/kg | kJ/kg | kJ/kg |                     |                          |                 |                   |
| pentane | 200.00| 56.71 | 470.37| 379.54| 33.53 | 42.73 | 0.337               | 0.656                    | 3.981           | 0.208             |
| R123    | 200.00| 46.29 | 455.50| 411.50| 251.06| 254.21| 0.212               | 0.679                    | 4.018           | 0.215             |
| R365mfc | 200.00| 127.36| 505.18| 452.27| 268.94| 279.29| 0.219               | 0.706                    | 4.063           | 0.224             |
| R141b   | 200.00| 39.44 | 535.56| 471.61| 257.83| 260.98| 0.234               | 0.726                    | 4.097           | 0.230             |
| R134a   | 200.00| 316.03| 487.52| 423.44| 271.62| 297.54| 0.233               | 0.936                    | 4.485           | 0.297             |

4. CONCLUSIONS

A thermodynamic criterion for selection of a fluid both for subcritical and supercritical organic Rankine cycle has been proposed. The postulated thermodynamic criterion will be quite helpful in preliminary scanning of different working fluids for selection to work in the micro CHP thermodynamic cycle. The criterion requires calculation of some non-dimensional numbers. The efficiency of the cycle is in a close relation to these numbers. Other criteria are also discussed. The ORC efficiency and sizes of heat exchangers seem to become the main future issues of such CHP units. The highest efficiency of the thermodynamic cycle is linked with the choice of the appropriate organic fluid, as well as temperatures higher than critical ones. The paper clearly shows that supercritical cycles exhibit higher efficiency than subcritical cycles. Improvement of about 5% in the overall efficiency was obtained for subcritical cycles. This was at the expense of a bigger vapour generator size. Therefore to sustain the compactness of heat exchangers more efficient heat exchangers should be built to operate with high performance in the vapour region, such as those with mini and microchannels. A further investigation of supercritical ORC seems to be challenging.

It results from the performed calculations that when pressure losses are not considered the best fluid applicable for successful application in micro CHP is ethanol and R141b in terms of efficiency and power available in turbine. Very promising seems to be the application of ethanol. In case of ethanol and R134a, the quality at the end of expansion process in turbine indicated only a small content of liquid present (x > 0.95), which increases the turbine life span. In case of other fluids the expansion process ends in the superheated steam region, requiring a regenerator to increase the efficiency of the cycle.

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Criteria for selection of working fluid in low-temperature ORC

SYMBOLS

- $c_p$: specific heat at constant pressure, J/kgK
- $d$: tube diameter, m
- $h$: enthalpy, kJ/kg
- $l$: cycle work per unit mass, kJ/kg
- $p$: pressure, Pa
- $Q$: rate of heat transferred, kW
- $q$: heat per unit mass, kJ/kg
- $T$: absolute temperature, K

Greek symbols

- $\eta$: cycle efficiency
- $\mu$: dynamic viscosity
- $\rho$: density

Subscripts

- $1$: state before expansion machine
- $2$: state after expansion
- $3$: state at outlet from condenser
- $4$: state after leaving the pump
- $c$: related to Carnot cycle
- $cr$: critical point
- $in$: input heat
- $lv$: related to latent heat of evaporation
- $out$: outlet

REFERENCES

Aghahosseini S., Dincer I., 2013. Comparative performance analysis of low temperature organic Rankine cycle (ORC) using pure and zeotropic working fluids. Appl. Therm. Eng., 54, 35–42. DOI: 10.1016/j.applthermaleng.2013.01.028.

Aljundi I.H., 2011. Effect of dry hydrocarbons and critical point temperature on the efficiencies of organic Rankine cycle. Renew. Energy, 36, 1196–1202. DOI: 10.1016/j.renene.2010.09.022.

Andersen W.C., Bruno T.J, 2005. Rapid screening of fluids for chemical stability in Organic Rankine Cycle applications. Ind. Eng. Chem. Res., 44, 5560–5566. DOI: 10.1021/ie050351s.

Bao J., Zhao L., 2014. A review of working fluid and expander selections for organic Rankine cycle. Renewable Sustainable Energy Rev., 24, 325–342. DOI: 10.1016/j.rser.2013.03.040.

Bertrand T.F., Papadakis G., Lambrios G., Frangoudakis A., 2008. Criteria for working fluids selection in low-temperature solar organic Rankine cycles. Proceedings Eurosun 2008, Lisbon, Portugal.

Braimakis K., Leontarits A-D., Preisinger M., Karellas S., Bruggeman D., Panopoulos K., Thermodynamic investigation of waste heat recovery with subcritical and supercritical low-temperature ORC based on natural refrigerants and their binary mixtures. Proceedings of ECOS 2014, the 27th Int. Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems, Turku, Finland.

Cho S.Y., Cho C.H., Ahn K.Y., Lee Y.D., 2014. A study of the optimal operating conditions in the organic Rankine cycle using a turbo-expander for fluctuations of the available thermal energy. Energy, 64, 900–911. DOI: 10.1016/j.energy.2013.11.013.

Drescher U., Bruggemann D., 2007. Fluid selection for the Organic Rankine Cycle (ORC) in biomass power and heat plants. Appl. Therm. Eng., 27, 223-228. DOI: 10.1016/j.applthermaleng.2006.04.024.

Garg P., Kumar P., Srinivasan K., Dutta P., 2013. Evaluation of isopentane, R-245fa and their mixtures as working fluids for organic Rankine cycles. Appl. Therm. Eng., 51, 292–300. DOI: 10.1016/j.applthermaleng.2012.08.056.
Hung T.C., 2001. Waste heat recovery of organic Rankine cycle using dry fluids. *Energy Convers. Manage.*, 42, 539–553. DOI: 10.1016/S0196-8904(00)00081-9.

Liu B.T., Chien K.H., Wang C.C., 2004. Effect of working fluids on organic Rankine cycle for waste heat recovery. *Energy*, 29, 1207–1217. DOI: 10.1016/j.energy.2004.01.004.

Mago P.J., Chamra L.M., Srinivasan K., Somayaji C., 2008. An examination of regenerative organic Rankine cycles using dry fluids. *Appl. Therm. Eng.*, 28, 998–1007. DOI: 10.1016/j.applthermaleng.2007.06.025.

Maizza V., Maizza A., 2001. Unconventional working fluids in organic Rankine-cycles for waste energy recovery systems. *Appl. Therm. Eng.*, 21, 381-390. DOI: 10.1016/S1359-4311(00)00044-2.

Mikielewicz D., Mikielewicz J., 2008. Cogenerative micro power plants – A new direction for development of power engineering? *Archives of Thermodynamics*, 29, 109-132.

Mikielewicz J, Mikielewicz D, 2009. Comparative study of selected fluids for use in supercritical Organic Rankine Cycles. *Archives of Thermodynamics*, 30, 3-15.

Nowak W., Borsukiewicz-Gozdur A., Stachel A.A., 2008. Using the low-temperature Clausius–Rankine cycle to cool technical equipment. *Appl. Energy*, 85, 582–588. DOI: 10.1016/j.apenergy.2007.09.001.

Rayegan R., Tao Y.X., 2011. A procedure to select working fluids for Solar Organic Rankine Cycles (ORCs). *Renew. Energy*, 36, 659–670. DOI: 10.1016/j.renene.2010.07.010.

Saleh B., Koglbauser G., Wendland M., Fisher J., 2007. Working fluids for low-temperature organic Rankine cycles. *Energy*, 32, 1210-1221. DOI: 10.1016/j.energy.2006.07.001.

Refprop 9.0, NIST software, 2010.

Tchanche B.F., Papadakis G., Lambrinos G., Frangoudakis A., 2009. Fluid selection for a low-temperature solar organic Rankine cycle. *Appl. Therm. Eng.*, 29, 2468-2476. DOI: 10.1016/j.applthermaleng.2008.12.025.

Wei D., Lu X., Lu Z., Gu J., 2007. Performance analysis and optimization of organic Rankine cycle (ORC) for waste heat recovery. *Energy Convers. Manage.*, 48, 1113–1119. DOI: 10.1016/j.enconman.2006.10.020

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