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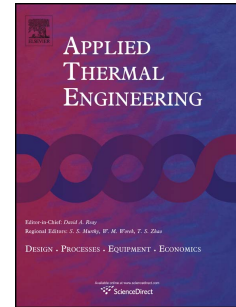
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A THERMODYNAMIC CRITERION FOR SELECTION OF WORKING FLUID FOR SUBCRITICAL AND SUPERCRITICAL DOMESTIC MICRO CHP

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Abstract

A thermodynamic criterion for selection of a fluid both for subcritical and supercritical organic Rankine cycle has been proposed. Theoretical performances of few fluids have been comparatively assessed for use in low-temperature domestic organic Rankine cycle micro systems. Of 20 fluids investigated, ethanol, R123 and R141b appear as the most suitable for small scale domestic CHP applications.

1. Introduction

In recent years there is observed a clear tendency, both worldwide and in the countries of European Union (EU), to increase the importance of so called dispersed generation, based on local energy sources and technologies utilizing both fossil fuels and renewable energy resources. Micro combined heat and power units (CHP) based on organic Rankine cycle (ORC) fit very well to that strategy and in recent years that technology has become a field of intense research. It appears as 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, such as for example solar power, biomass combustion, ground heat source or waste heat. Unlike in the steam power cycle, where vapour of water is the working fluid, ORC employ refrigerants, hydrocarbons, solvents or other organic substances.

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 the ORC systems. Some of the mentioned above technologies are mature and have demonstrated their potential performance and production costs, whereas others are at their earliest stages of market entry and are still relatively expensive and may not perform to their expected potential. The ORC technology is currently produced in small amount, but is likely to become significantly cheaper over the next few years as it enters mass production. Authors are at the moment involved in a large scale national project with the objective to develop a commercially available ORC CHP unit for domestic applications. That technology is also 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 commercially available. With the advent of these technologies the (electrical) efficiency levels, currently at around the 10% mark, are likely to rise considerably to reach 25%. It must be remembered, however, that new technologies, especially those based on fuel cells, will reach even higher efficiencies in the next decade or so. They are expected to achieve electrical conversion efficiencies of over 40%. In case of ORC units the power of expanding device of CHP ranges from a few to tens of kilowatts.

Considered here will be application of ORC CHP unit in small households, where the turbine or other expanding machine power will be of the order of 3-4kW. That amount of power for the single household is regarded sufficient, Norgaard and Skytte 2009 [16]. Primary energy in such CHP is better utilized than in units producing electricity only. CHP unit utilizes the energy of fuel, in almost 85-95%. About 70 of energy is delivered as heat, and about 15 to 25% is additional production of electric energy, see Fig. 1. Professional power plants producing electricity, in some cases, achieve the rate of conversion of over forty few percents. In the near future expected are cycles with efficiency exceeding 50%. Nevertheless, there ought to be included transmission losses, which permit to say that the micro CHP units, planned to be

developed in the near future, are quite promising technologies. Literature sees several studies where different micro-ORC systems designed for heat production and electricity generation were studied, see for example Nguyen et al. [1], Saitoh et al. [2], Lemort et al. [3]. There are still issues requiring particular attention in appropriate implementation of that technology in practice, namely the expansion device, which in the above cases was a modified scroll compressor to the expansion mode. The small size of the expansion device is a demanding challenge to overcome as the rotating shaft attains very significant velocities which makes it difficult to select appropriate electricity generator. Authors are involved at the moment in a development of a turbine for implementation in a micro CHP.

Another issue which seems not to be definitely clarified in the literature is the selection of the relevant organic fluid suitable for the micro ORC cycle. The information regarding that topic is not complete and does not show how to appropriately select a good working fluid to specified conditions. The economics of a 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. There are examples of papers regarding selection of the fluid for waste heat applications [4,6], solar installations [3,5]. Some selection criteria have been put forward by various authors [7-11], incorporating thermodynamic properties, provided in literature but these do not have a general character. After these papers the expected features of a good fluid are: low specific volumes, high efficiency of thermodynamical cycle, high latent heat, moderate pressures in the heat exchangers, low cost, low toxicity, low ODP and low GWP among others. The latter is due to the fact that most of refrigerants are contributing to the ozone depletion. However, not all the considered substances in the paper fall into that category and the ones selected for the present study are to be in use until 2030.

Apart from the issues outlined above, the up to date research was focused mainly on subcritical cycles. There is, however, also an unexplored area of supercritical parameters which could offer also great opportunities for exploration. The analysis of supercritical fluid parameters may even lead to higher efficiencies making the micro CHP more attractive. Steam supercritical cycles attract more attention from the professional power cycles point of view but in case of low-boiling point fluids point of view there are no actions in that direction. It must be noted that the critical point of organic fluids is reached at much lower pressures and temperatures compared with steam. Therefore supercritical fluid parameters are much easier to be realized in practical applications in these cases than in case of water. However, there is some limitation in case of domestic micro CHPs. The objective for a domestic micro CHP is also to design small sized heat exchangers and for that reason not all supercritical fluids could be suitable. It is well known that heat transfer to gases is much less efficient than to two-phase fluids and that leads to excessive sizes of heat exchangers.

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, etc, 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 resistances. The criteria developed have a much wider application and can be used for other temperature ranges also.

2. Literature review on working fluid selection

There is a wide selection of organic fluids, which can generally be used in ORC systems. For example Mago et al., 2007 [12], conducted investigations with different organic fluids for systems with heat recovery. They concluded that 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.

In their opinion the refrigerants are most promising fluids for ORC cycles, especially with the view of their low toxicity. That is unfortunately not in line with International protocols which pushed researchers to investigate new environmentally friendly fluids which could serve as substitutes. Contributing in this direction, performance of carbon dioxide, synthetic and refrigerant mixtures in different types of cycles are being examined by various researchers, [7-12]. Especially CO₂ is expected to be a long term substitute and a major fluid in refrigeration and air-conditioning. The biggest problem with its implementation are however high pressures corresponding to temperatures required by a considered in the paper CHP. For the conditions considered here we would have to deal with CO₂ gas cycles, which was not the intention.

Another characteristic feature, important in selection of a fluid, is the boiling curve at a specified saturation temperature. That feature has a particular influence on the restrictions in application of a fluid in thermodynamical cycles (cycle efficiency, heat exchanger sizes). The slope of the saturated vapour curve in T-s diagram depends on the type of applied working fluid. We discern here three possible cases, namely the isentropic, dry and wet fluids, Fig. 2. The dry fluid features a positive slope of the saturated vapour curve, the wet one – negative, whereas the isentropic fluid features practically a vertical saturation curve ($\text{tg}\alpha=90^\circ$). Dry and isentropic fluids exhibit better thermodynamic efficiencies of expansion devices, as there are no liquid droplets in the turbine, contrary to wet fluids. On the other hand they require larger heat transfer surfaces. In

case of dry fluids usually a regenerator is required. The dry fluids used in Maizza [6], investigations were R113, R123, R245ca and isobutane. It has been concluded that the refrigerant R123 is the best fluid.

In a concept of the micro heat and power plant which would be used for production of electricity and heat in households or small enterprise, the heat transfer would take place in a boiler, where a thermal oil will be heated to a temperature below 620K. In such systems we are interested in attaining the highest possible energy conversion into electricity and internal efficiency of vapour turbine. The increase of the upper temperature of the cycle is directly responsible for that. In case of analysis of subcritical cycles such fluids have been selected for the analysis where critical temperature is greater than 150°C, and critical pressures are below 30bar. The following fluids have been selected for the preliminary analysis: ammonia, perfluorobutane C₅F₁₂, methanol, ethanol, heptane, isohexane, R11, R12, R123, toluene, R152, R134a, R141b, R227, R245ea, R245ca, R365mfc, SES36 and water. SES36 is an azeotropic mixture of Solkane R365mfc which boils at 36.7°C. Figure 3 and 4 present the liquid and vapour saturation curves for a selection of fluids in p-v and T-s coordinates, D. Mikielewicz and J. Mikielewicz, 2008 [13].

3. Selection of working fluid for micro ORC installation - thermodynamical criterion

Following our experience, J. Mikielewicz and D. Mikielewicz, 2009 [14], the simplest configuration of Rankine cycle was analysed. 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.

The fluids are featuring, in general, all possibilities of the slope of saturated steam line, namely a positive slope of saturated vapour line (SES 36, R365mfc), a negative slope (ethanol, R134a) and

almost isentropic distribution of temperature versus entropy (R141b), Fig. 3 and Fig. 4. That has a bearing on the course of expansion line meaning that the expansion in the first case is all the way through the superheated steam region, in the second one it proceeds in the wet steam region, whereas in the third one, partially in the wet region and finally terminating just in the superheated steam region.

It is apparent that heat transfer to vapour exhibits smaller values of heat transfer coefficient than in the case of heat transfer during boiling of vapour and therefore influences the size of heat exchangers. Small dimension of heat exchangers (condenser and evaporator channels) requires also analysis of pressure drops in these exchangers, which influence cycle parameters and as a consequence temperature differences in heat exchangers and also the heat exchanger dimensions. In such case calculations of thermodynamic cycle parameters are rather tedious and iterative.

In calculations it has been assumed that vapor parameters at turbine inlet are known, namely (p_1 , T_1), as well as temperatures of cooling liquid at inlet and outlet to the evaporator (T_{1w} , T_{2w}). The term turbine is used here as the traditional Clausius-Rankine cycle uses that device for expansion. Thermal oil is heated in the boiler to the temperature of 320°C which is subsequently giving its heat away in the heat exchanger to convert the organic fluid from liquid state to the vapour state (parameters (p_1 , T_1)). These parameters correspond to temperature of 170°C and related pressure. A number of fluids had been examined for the case of subcritical parameters. In such case expansion starts at vapour saturation line and proceeds isentropically to the pressure corresponding to 50°C. Some of these conditions correspond to wet vapour region (water, ethanol) whereas some of them are in the superheated vapour region, see Fig. 5. Similarly, a number of fluids was examined for their performance in case of supercritical parameters. In the latter case $T_1=200^\circ\text{C}$ and pressure is related to that temperature in such a way that the expansion process terminates isentropically at the vapour saturation line corresponding to temperature of

50°C, see and Fig. 6. Oil temperature at outlet from the heat exchanger has temperature of 280°C. Efficiency of turbine $\eta_T=1$ has been assumed. The demand for heat has been regarded as known (heat exchanged in the condenser is equal to 20kW). The condensation temperature results from the required parameters of central heating installation. In the considered case condensation temperature of 50°C has been assumed.

As mentioned earlier, in the case of micro-CHP the electricity production is somewhat a side product in production of heat and therefore the heat energy is the main output of the thermodynamic cycle. Assumption of heat demand enables us to compare various working fluids and evaluate the possibility of production of electricity at the same production of heat. In calculations it has been assumed that the heat exchangers (boiler and condenser) are efficient compact units. In the development of the prototype of such unit the shell-and-tube type heat exchangers are envisaged which utilize minichannels. In such configuration both condensation and evaporation is assumed to occur inside the tubes. In figure 5 a simplified schematic of the micro-CHP is presented.

In the course of quantitative selection of appropriate fluids for operation at sub- and supercritical parameters simple analysis has been carried out. It resulted in development of a criterion for finding of a fluid having a high efficiency. The analysis commences with the expression for the cycle overall efficiency:

$$\eta = \frac{l_{\text{cycle}}}{q_{\text{in}}} = \frac{h_1 - h_2}{h_1 - h_3} \quad (1)$$

In relation (1), for simplicity, enthalpy change due to the presence of pump has been neglected, i.e. $h_3 \approx h_4$. Enthalpies can be written in terms of temperatures and fluid properties. In the case of a subcritical cycle the terms of a corresponding liquid saturation state yields:

$$h_1 = h_3 + c_p(T_1 - T_2) + h_{lv}(T_1) \quad (2)$$

On the other hand, in case of a supercritical cycle that is:

$$h_1 = h_3 + c_p(T_1 - T_2) \quad (3)$$

In (2) and (3) specific heat c_p is regarded as a mean specific heat between states 1 and 3. In both cases the enthalpy at the end of expansion yields:

$$h_2 = h_3 + x_2 h_{lv}(T_2) + \Delta h_{\text{superheat}} \quad (4)$$

Relation (4) is a general formula describing the state after the expansion in turbine or other expansion machine. In case of expansion of dry fluids, the vapour superheat, $\Delta h_{\text{superheat}}$, is present and then the quality $x=1$ (state 2 is found in the superheated vapour region), whereas in case of expansion of wet fluids the final state has some quality x and $\Delta h_{\text{superheat}}=0$. In general, two latter cases in relation [4] can be combined to yield a formulae:

$$h_2 = h_3 + \Delta H(T_2) \quad (5)$$

In (5) $\Delta H=x_2 h_{lv}$ or $\Delta H=h_{lv}(T_2)+\Delta h_{\text{superheat}}$. Substituting relations (3) to (5) into (1) we obtain the cycle efficiency. In case of subcritical cycle it yields:

$$\eta = \frac{h_3 + c_p(T_1 - T_2) + h_{lv}(T_2) - h_3 - \Delta H(T_2)}{h_3 + c_p(T_1 - T_2) + h_{lv}(T_1) - h_3} = 1 - \frac{\Delta H(T_2)}{c_p(T_1 - T_2) + h_{lv}(T_1)} \quad (6)$$

In case of supercritical case, when temperature of vapour leaving the evaporator T_1 prior to entering the expansion machine is greater than critical temperature T_{cr} for a given fluid, it is:

$$\eta = \frac{h_3 + c_p(T_1 - T_2) - h_3 - \Delta H(T_2)}{h_3 + c_p(T_1 - T_2) - h_3} = 1 - \frac{\Delta H(T_2)}{c_p(T_1 - T_2)} \quad (7)$$

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

$$\eta = 1 - \frac{\frac{\Delta H(T_2)}{h_{lv}(T_1)}}{\frac{c_p T_1}{h_{lv}(T_1)} \eta_c + 1} = 1 - \frac{\frac{\Delta H(T_2)}{h_{lv}(T_1)}}{Ja(T_1) \eta_c + 1} \quad (8)$$

where: $Ja = c_p T / h_{lv}$. The term $c_p T / h_{lv}$ has been named the Jakob number due to its close similarity to the original definition of the Jakob number. In case of the supercritical cycle:

$$\eta = 1 - \frac{1}{\frac{c_p T_1}{\Delta H(T_2)} \eta_c} = 1 - \frac{1}{Ja(T_1, T_2) \eta_c} \quad (9)$$

Analysis of (8), valid for a subcritical cycle, enables to conclude that the overall cycle efficiency

is a function of a ratio $\Delta H(T_2) / h_{lv}(T_1)$ and the Jakob number, defined as $Ja(T_1) = \frac{c_p T_1}{h_{lv}(T_1)}$, for the

determined Carnot efficiency. It stems directly from (8) that we should consider the ratios of

$\Delta H(T_2) / h_{lv}(T_1)$ and $c_p T_1 / h_{lv}(T_1)$ when we want to consider a substance as a working fluid in the

subcritical cycle from the efficiency point of view. The smaller the value of the ratio of these two

terms the higher is the efficiency obtained by the working fluid in the cycle. General properties

of selected five fluids for the final inspection are presented in Table 1. Properties were calculated

using Refprop 8.0 software [15]. Sample calculations for several fluids for the subcritical

conditions have been presented in Table 2. We can notice from there that the criterion is

reflecting the ratio of $\Delta H(T_2) / h_{lv}(T_1)$ and $c_p T_1 / h_{lv}(T_1)$. 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 (9) 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 highest possible values, i.e. the higher the value

of Jakob number $Ja(T_1, T_2)$ the resulting thermal efficiency is higher. Calculations for that case

are presented in Table 3. 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 $\Delta H(T_2)/h_{lv}$ in case of supercritical cycle.

Presented criterion points that the best one from those considered thus far is R141b and ethanol. Apart from the postulated thermodynamical 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.

5. Conclusions

Thermodynamic characteristics and performances of different fluids were analyzed for selection as working fluids in a low-temperature organic Rankine cycle for domestic applications. A thermodynamic criterion for selection of a fluid both for subcritical and supercritical organic Rankine cycle has been proposed. Theoretical performances of few fluids have been comparatively assessed for use in low-temperature domestic organic Rankine cycle micro systems. Of 20 fluids investigated, ethanol, R123 and R141b appear as the most suitable for small scale domestic applications. 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, Tables 2 and 3.

The ORC efficiency and sizes of heat exchangers seems 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. In the paper is clearly shown that supercritical cycles exhibit higher efficiency than the subcritical cycles. Improvement is about 5% in the overall efficiency referred to subcritical cycles. This is at the expense of a bigger vapour generator size. Therefore to sustain the compactness of heat

exchangers it is required that more efficient heat exchangers should be built to operate with high performance in the vapour region, such as for example the ones utilizing the mini and microchannels.

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Nomenclature

c_p - specific heat at constant pressure, J/kgK

d - tube diameter, m

G - mass velocity, kg/m²s

h - enthalpy, kJ/kg

l - cycle work per unit mass, kJ/kg

p - pressure, Pa

q - heat per unit mass, kJ/kg

T - absolute temperature, K

w - flow velocity, m/s

x - quality,

Greek symbols

η - cycle efficiency

μ - dynamic viscosity

ρ - density

ξ - friction coefficient

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
- L - liquid
- LO - liquid only
- lv - related to latent heat of evaporation

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Figure captions:

Fig. 1. A general schematic of a domestic micro CHP.

Figure 2: Comparison of cycles for different working fluids: a) ideal one – expansion proceeds along the vertical and isentropic saturated vapour line (isentropic fluid), b) „wet” and c) „dry”.

Fig. 3. Comparison of critical pressures for different fluids with respect to their application to ORC.

Fig. 4. Comparison of critical temperatures of different fluids with respect to their possible application in ORC.

Fig. 5. Schematic of micro-CHP thermodynamic Rankine cycle.

Fig. 6. Schematics of subcritical (a) and supercritical (b) cycles.

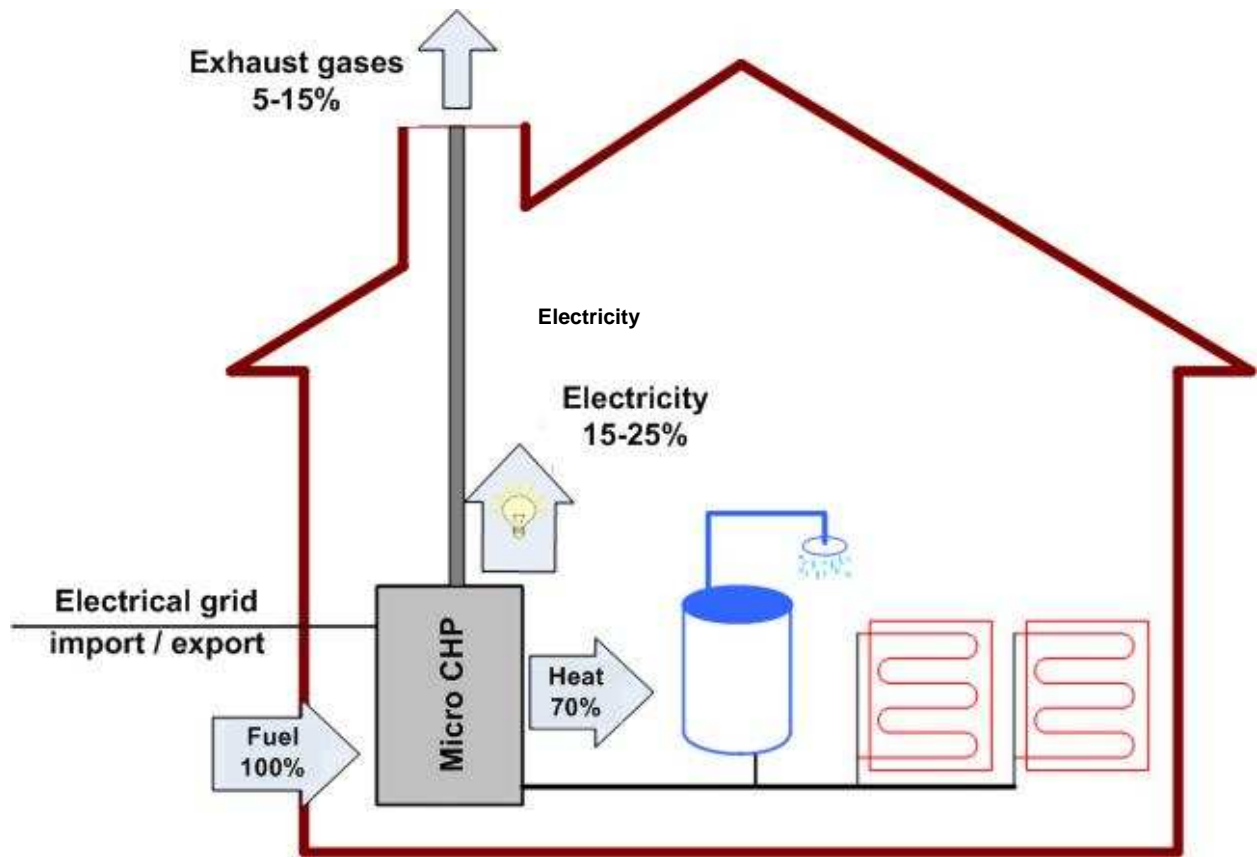
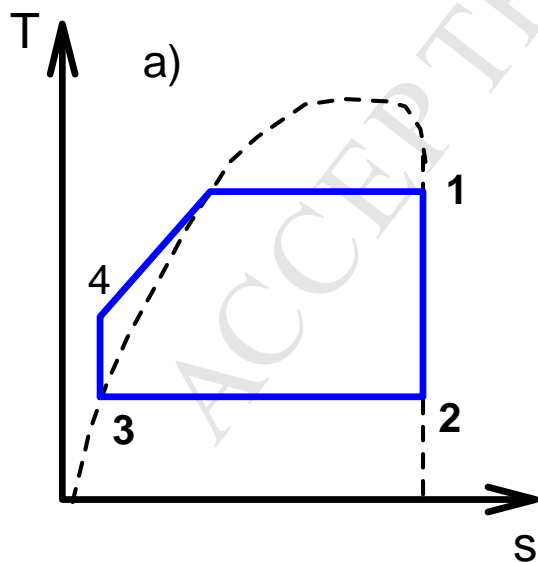


Fig. 1. A general schematic of a domestic micro CHP.



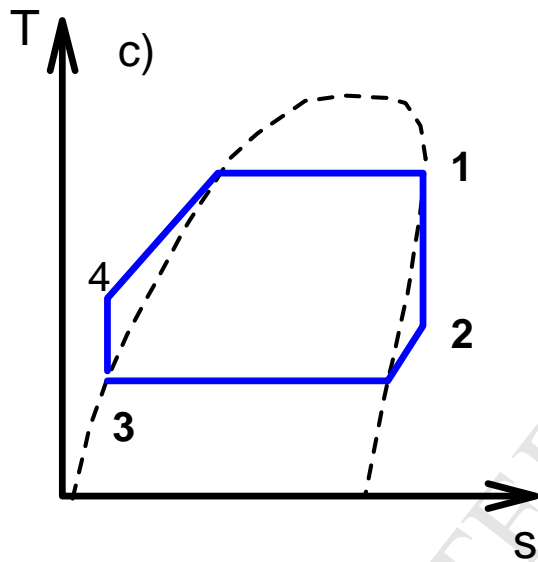
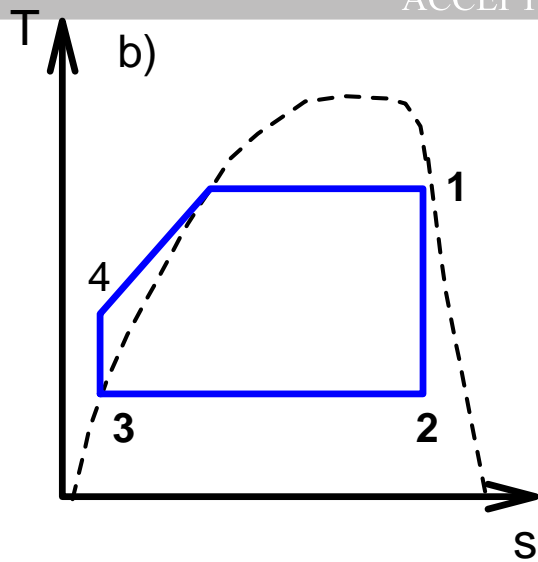


Fig. 2: Comparison of cycles for different working fluids: a) ideal one – expansion proceeds along the vertical and isentropic saturated vapour line (isentropic fluid), b) „wet” and c) „dry”.

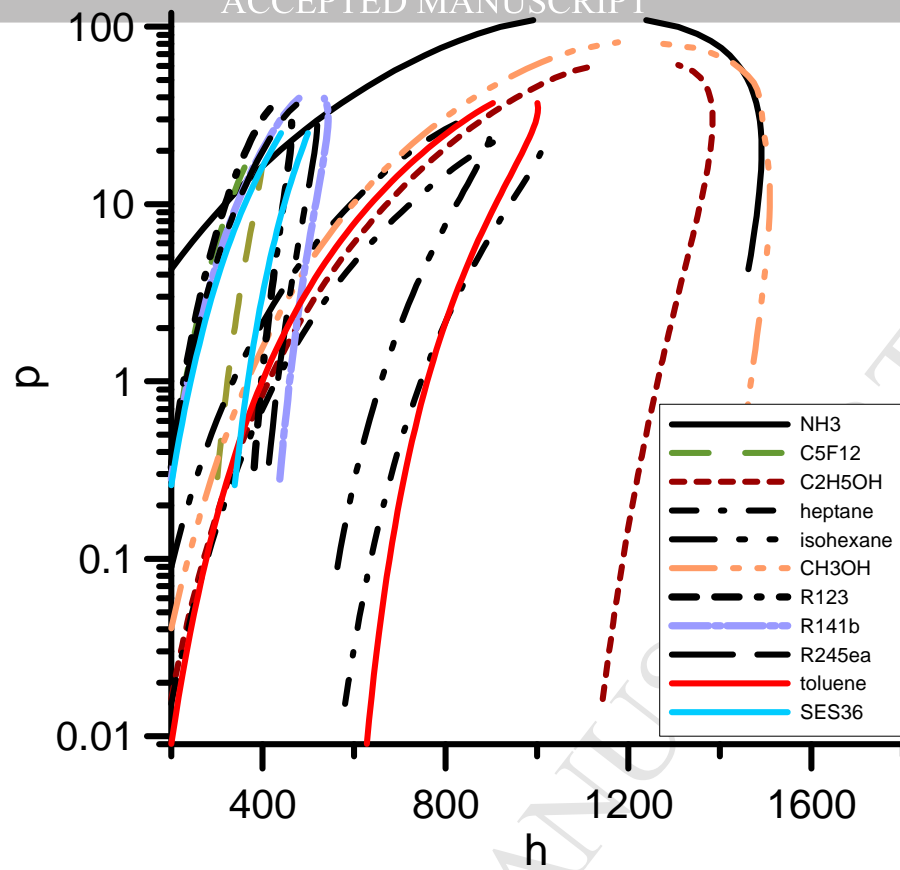


Fig. 3. Comparison of critical pressures for different fluids with respect to their application to ORC.

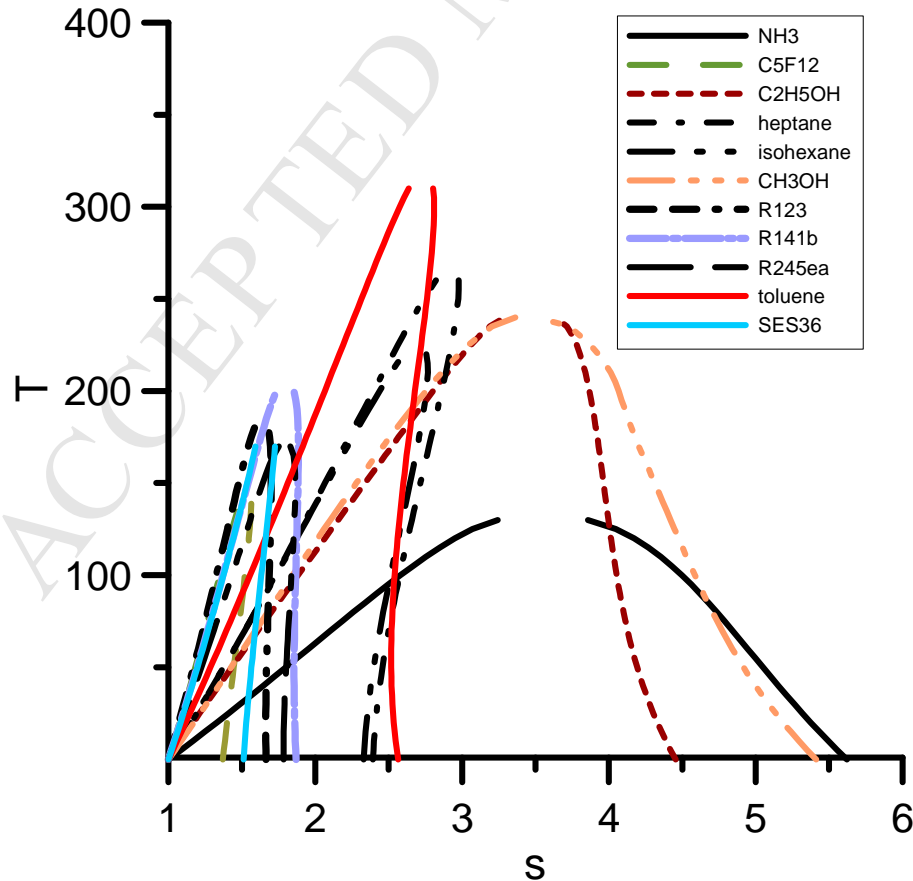


Fig. 4. Comparison of critical temperatures of different fluids with respect to their possible application in ORC.

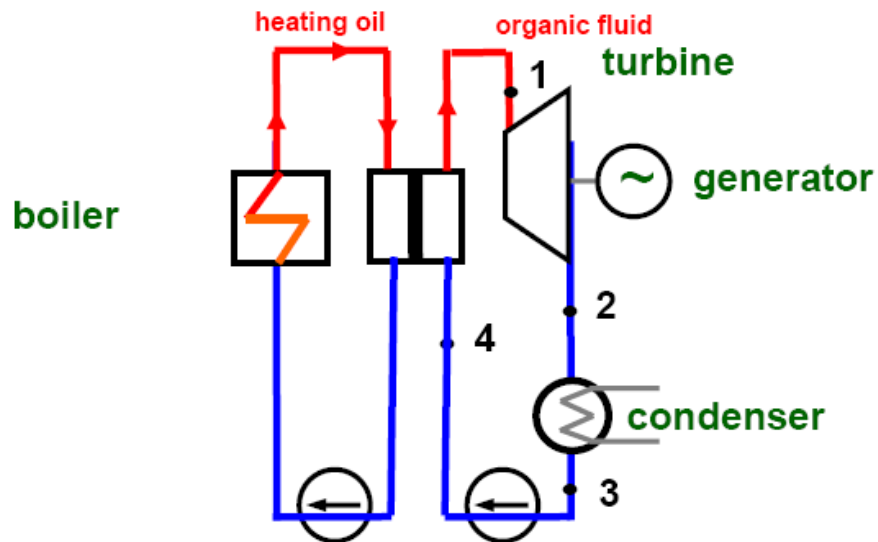


Fig. 5. Schematic of micro-CHP thermodynamic Rankine cycle.

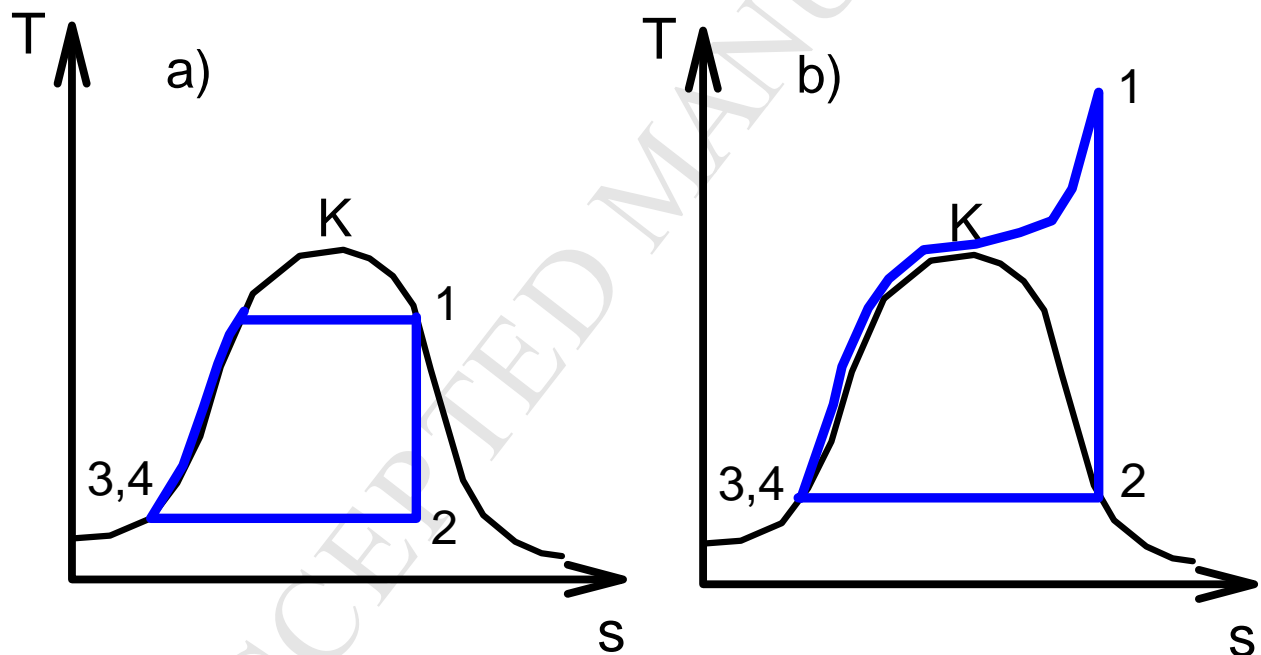


Fig. 6. Schematics of subcritical (a) and supercritical (b) cycles.

Fluid	M kg/kmol	p_{cr} bar	T_{cr} °C	p_{cond} bar
R365mfc	148.07	32.66	186.85	1.42
R123	152.93	36.74	183.79	2.14
R141b	116.95	42.12	204.35	1.83
C ₂ H ₅ OH	46.00	61.48	240.75	0.30
R134a	102.03	40.593	101.06	13.18

Table 1. Characteristics of considered fluids.

Fluid	T ₁	P ₁	h ₁	h ₂	h ₃	h ₄	η_{th} (eq.1)	$\eta_b = \eta_{th}/\eta_c$	Ja(T ₁)	$\Delta H(T_2)/h_{lv1}$	η_{th} eqn 8
	°C	bar	kJ/kg	kJ/kg	kJ/kg	kJ/kg	-	-	-	-	-
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

Table 2. Characteristics of cycle efficiencies for the case of subcritical cycle parameters, Carnot efficiency $\eta_c=0,271$.

Fluid	T ₁	P ₁	h ₁	h ₂	h ₃	h ₄	η_{th} (eq. 1)	$\eta_b = \eta_{th}/\eta_c$	Ja(T ₁ , T ₂)	η_{th} eqn 9
	°C	bar	kJ/kg	kJ/kg	kJ/kg	kJ/kg	-	-	-	-
pentane	200,00	56,718	470,37	379,54	33,53	42,733	0,337	0,656	3,981	0,208
R123	200,00	46,288	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	39,441	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

Table 3. Characteristics of cycle efficiencies for the case of supercritical cycle parameters, Carnot efficiency $\eta_c=0,317$.