Thermodynamic investigation of waste heat recovery with subcritical and supercritical low-temperature Organic Rankine Cycle based on natural refrigerants and their binary mixtures

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Abstract:
The Organic Rankine Cycle (ORC) is widely considered as a very promising technology in the field of low temperature waste heat-to-power conversion and has already been implemented in various industrial scale applications. This work aims to investigate the waste heat recovery (WHR) potential from low grade industrial processes using the ORC and some of its innovative variations, such as the cycle operation under supercritical pressures and the use of binary zeotropic working fluids. Moreover, the options considered in the present work focus on the use of low ozone depletion and global warming potential (ODP and GWP) natural hydrocarbon refrigerants (pentane, hexane, and others) which are a cheap alternative to fluorinated gases. A series of simulations are performed for three heat source temperature levels (150, 225 and 300 °C) and the optimal working fluids and operating conditions are identified. Meanwhile, some important technical parameters are estimated (turbine size parameter, volume flow ratio, rotational speed, UA values in heat exchangers etc.) in each case. The performance improvement that can be achieved with the supercritical ORC and the use of binary mixture working fluids depends on the temperature of the heat source. Compared to the optimized subcritical ORC with R245fa as a working fluid, Propane90/Butane10 leads to an efficiency improvement of 80% under subcritical operation at 150 °C. At 225 °C, the exergetic efficiency of the supercritical ORC of Butane40/Propane60 is 58% higher compared to that of the subcritical R245fa, while at 300 °C the respective improvement that is attained by Butane50/Cyclopentane50 is roughly 60%. Concerning the technical evaluation parameters of the cycle, in the lower temperatures the natural refrigerants and their mixtures have equivalent or even improved UA values, turbine size parameters and volume flow ratios, while R245fa has in general lower rotational speeds. At 300°C, on the other hand, the use of R245fa is associated with substantially favorable technical characteristics despite its inferior thermodynamic performance.

Keywords:
Waste heat, supercritical, natural refrigerants, zeotropic mixtures, efficiency increase, Organic Rankine Cycle

Nomenclature
\textbf{A} \quad \text{heat exchanger surface area, m}^2
\textbf{\dot{E}} \quad \text{exergy, kWe}
\textbf{GWP} \quad \text{global warming potential (relative to carbon dioxide)}
\textbf{h} \quad \text{specific enthalpy, kJ/kg}
\textbf{I} \quad \text{irreversibility, kWe}
LMTD logarithmic mean temperature difference

\( \dot{m} \) mass flow rate of the working fluid, kg/s

\( n \) rotational speed (RPM)

ODP ozone depletion potential (relative to R-11)

\( p \) pressure, bar

\( P \) power, kW

\( \dot{Q} \) heat flow, kWth

\( s \) specific entropy, kJ/kgK

SP size parameter of turbine, m

\( T \) temperature, °C

U overall heat transfer coefficient, kW/K

\( \dot{V} \) volume flow rate of the working fluid, m³/h

VFR volume flow ratio of expander inlet and outlet streams

**Greek symbols**

\( \Delta \) difference

\( \eta \) efficiency

**Subscripts**

0 ambient

cond condenser

crit critical

CW cooling water

el electric

ex exergetic

exp expander

G generator

glide temperature glide

gross gross electricity

heat heater

HS heat source

in inlet

is isentropic

lm logarithmic mean

m mechanical

M motor

net net electricity

ORC working fluid of ORC

out outlet

pump pump

th thermal
1. Introduction

1.1. Potential of the ORC for waste heat recovery

Low and medium grade waste heat utilization for electricity production has attracted significant interest as a means to alleviate the energy shortage and environmental pollution problems associated with excess CO₂ and other air pollutants (NOₓ, SOₓ etc) emissions [1]. Most typical sources of abundant waste heat can be found in industrial processes of steel, cement, glass, oil and gas [2]. Schuster et al. report [3] that the heat rejected by various industrial processes can surpass 50% of the total initial heat produced. Additionally, remarkable amounts of waste heat are carried by exhaust gases that are rejected from internal combustion engines [4]. Campana et al. [2] have assessed the potential of electricity generation from waste heat in Europe and have estimated that a total of 21.6 TWh can be produced on an annual basis, with savings amounting to 1.95 billion € and 8.1 million tonnes of Greenhouse Gas (GHG) emissions. Considering the above, it becomes evident that, apart from its positive environmental impact, waste heat recovery (WHR) for the production of electricity can lead to considerable economic benefits for the relevant industries, by helping reduce energy demands and subsequently allow to decrease fuel consumption costs.

The Organic Rankine Cycle (ORC) has been repeatedly proposed and extensively investigated as an appealing technology for WHR-to-power applications [5-9]. It is also already a widespread technology as a bottoming cycle for geothermal applications and biomass fired power plants [10, 11]. Hajabdollahi et al. [6] modelled and optimized an ORC for diesel engine waste heat recovery and identified R123 and R245fa as the best working fluid candidates from a thermo-economic standpoint. Quoilin et al. [7] developed a thermo-economic model for evaluating WHR-ORCs. By comparing a number of refrigerants under varying operational conditions, he stressed that the thermo-economic and the thermodynamic optimization of WHR-ORC systems may give different results. Wei et al. [8] underlined the importance of maximizing the utilization of the heat source for increasing the power output of the ORC. Dai et al. [9] compared the conventional water-steam Rankine cycle with the ORC for low grade (145 °C) heat sources. He concluded that the ORCs are more efficient, with R236EA exhibiting the highest exergy efficiency among the working fluids that he examined.

Some of the ORC’s primary advantages against the conventional steam-water Rankine cycle include its capability to operate at very low temperatures, reduced cost, smaller component size and simplicity of construction and operation [1, 5, 12]. Two of the main operating parameters affecting the overall thermodynamic efficiency and cost competitiveness of ORC applications are the working fluid and its evaporation pressure/temperature [7].

1.2. Working fluids and efficiency improvement strategies

There is a wide variety of organic fluid candidates for ORC systems, including hydrocarbons, hydrofluorocarbons, hydrochlorofluorocarbons, perfluorocarbons, siloxanes etc [12]. Although many studies have focused on the selection of the most appropriate ones [1, 13, 14], no single fluid has been identified as ultimately optimal for all ORCs. This is in part due to the variability of the characteristics (temperature profile ranges, physicochemical properties etc.) of the several heat sources considered. Furthermore, it can be also attributed to the different cycle working conditions that are assumed in each case, as well as to the different indicators used by various researchers for evaluating the system performance [14].

So far a number of refrigerants have been already banned or are to be phased out in the proximate future, in accordance with legislation (e.g. Montreal Protocol [15] and Kyoto Protocol [16]) aiming to restrict the use of high Ozone Depletion Potential (ODP) and Greenhouse Warming Potential (GWP) fluids. The European Union through a series of regulations [17, 18] aims to progressively decrease the production of certain fluorinated gases (F-gases) by 80% of today’s level until 2030. Because of the above legal restrictions, the price of typically used ORC-fluids, such as R245fa is expected to increase dramatically. The result is a shift of interest towards the use of low ODP and
GWP natural refrigerants (such as butane, pentane, hexane etc.) as working fluids. These refrigerants are available at low prices and are viewed as promising options concerning the overall system efficiency of the ORC. However, a major safety issue concerning their use in ORC systems is their high flammability and the consequent explosion risk. Therefore, the design and operation of such systems requires special attention.

Meanwhile, a number of studies have suggested that the ORC energy and exergy efficiency can be further improved when the working fluid is pumped to supercritical pressures before it is heated to its maximum temperature [19-21]. The main concept behind the application of the supercritical ORC relies on the expected minimization of the exergy destruction losses during the heating of the supercritical working fluid, which takes place under a variable temperature (contrary to the evaporation which occurs isothermally). Schuster et al. [19] showed that for a number of working fluids, the supercritical ORC can lead to an increase of the thermal and overall system efficiency of waste heat applications to up to 8%. According to Vetter et al. [20], who performed thermodynamic simulations considering a large number of working fluids, an increase in both thermal efficiency and net power output for low enthalpy (~150-170 °C) processes is achieved under supercritical operation of the cycle. Mikielewicz et al. [21] reports that through the implementation of the supercritical ORC, an overall efficiency improvement of roughly 5% can be attained in micro CHP applications. Despite these potential efficiency benefits, however, it should be noted that in supercritical conditions, the necessary heat exchanger surface is generally larger [22], and thus the heat exchange equipment may be more costly and require rigorous design.

Another possible improvement of the ORC is the replacement of pure substances with zeotropic mixtures as working fluids for the cycle [1, 23, 24]. Contrary to pure fluids, the subcritical isobaric phase change of these mixtures takes place non isothermally. The temperature glide of the working fluid during its evaporation and condensation permits a better matching of its temperature with the temperature of the heat source (evaporator) and the cooling medium (condenser). This, in turn, provides the opportunity to reduce the irreversibility that occurs in these process steps of the ORC and increase the exergetic efficiency of the system [23-25]. Heberle et al. [23] examined the potential of R227ea/R245fa and isobutene/isopentane mixtures for low temperature geothermal applications. He estimated that the use of these zeotropic mixtures can lead to an increase in the exergy efficiency from 4.3 to 15% compared to their most efficient pure components. Liu et al. [24] explored the thermodynamic performance of a number of zeotropic mixtures. Like Heberle et al. [23], he emphasized the matching of the temperature glide during the condensation of the working fluid with the temperature change of the cooling medium as an optimization criterion for estimating the ideal concentration of the mixture components. A detailed thermodynamic and economic comparison between the use of fluid mixtures and the supercritical ORC for geothermal waste heat utilization is given in [26].

### 1.3. Objectives of the present work

The present work and has a dual purpose. Firstly, it aims to evaluate the performance of the WHR-ORC when using natural hydrocarbons as working fluids. The second goal is to investigate the potential increase of the cycle efficiency by using binary zeotropic mixtures consisting of pure natural refrigerants. In both cases, the operation under subcritical and supercritical pressures is simulated by thermodynamically modelling the WHR-ORC system. The significance of this paper can be summarized in the following points. To begin with, given the advantages of the natural hydrocarbons against artificial refrigerants regarding their cost, environmental behaviour and safety, it is very interesting to further evaluate their attractiveness as working fluids candidates for the ORC based on their thermodynamic behaviour. Secondly, the work aims to assess two of the most promising improvements of the ORC for these natural hydrocarbons: the supercritical operation and the use of working fluids consisting of binary zeotropic mixtures. Most importantly, to the knowledge of the authors, the combined effect of supercritical operation pressures and the use of binary mixtures in the ORC has not yet been investigated.
2. Methodology and assumptions

2.1. System description

For the numerical simulations performed in the study, a generic heat source stream consisting of dry atmospheric air is assumed. The saturated liquid refrigerant is pressurized with a pump. A heat exchanger is used for transferring the energy content of the heat source to the working fluid. Due to the relatively low heat source temperatures considered in the present study, the heat exchange between the waste heat stream and the working fluid takes place directly, without the integration of an intermediate heat transfer loop, which is a fairly common practice in WHR applications. Depending on the maximum operational pressure of the cycle, the working medium is introduced to the expander either as saturated vapour or at supercritical state. No superheating is deemed necessary for the fluids investigated (except for Propane), since the slope of the saturation curve in the T-S diagram has a negative value (dry fluids) and therefore no liquid phase occurs at the expander outlet.

Fig. 1. Schematic process scheme of the WHR-ORC investigated

Following the expansion process, the superheated fluid stream flows through the condenser, where it is cooled down by a stream of cooling water. The condensed saturated liquid re-enters the pump, repeating the cycle (Fig. 1).

The simulations of the thermodynamic cycle and the calculations of all thermophysical properties were carried out using the AspenPlus™ software by using the Peng-Robinson equation of state with Boston-Mathias alpha function property method [27]. A steady state operation is assumed, while the heat and pressure losses through piping, fittings and heat exchangers are considered equal to zero.

2.2. Performance evaluation parameters

During the expansion process of the working medium, an amount of power $P_{\text{exp}}$ is produced in the turbine.

$$P_{\text{exp}} = m_{\text{ORC}} (h_2 - h_3)$$  (1)

The mechanical efficiency $\eta_m$ is used to represent the percentage of $P_{\text{exp}}$ that is lost due to friction losses in the shaft and the gearbox that connect the expander with the rotor of the electric generator. Additional power losses occur during the conversion of the mechanical power of the shaft to electricity in the generator. These losses are indicated by the generator efficiency $\eta_G$. The gross electricity produced by the WHR-ORC is thus given by the equation:
\[ P_{el, gross} = \eta_m \eta_G P_{exp} \]  
\( (2) \)

A part of the gross electricity is used for powering the motor of the pump. During the pressure change of the working fluid in the pump, it absorbs an amount of power given by the equation:
\[ P_{pump} = \dot{m}_{ORC} (h_1 - h_2) \]  
\( (3) \)

Assuming a motor efficiency \( \eta_M \) accounting for the power losses during the conversion of electricity to mechanical work in the pump, the electric power required by the pump is:
\[ P_{el, pump} = \frac{\dot{m}_{ORC} (h_1 - h_2)}{\eta_M} \]  
\( (4) \)

The net electricity produced by the system is therefore equal to:
\[ P_{el, net} = P_{el, gross} - P_{el, pump} = \eta_m \eta_G P_{exp} - P_{pump} = \dot{m}_{ORC} \left[ \frac{\eta_m \eta_G (h_2 - h_3) - (h_1 - h_2)}{\eta_M} \right] \]  
\( (5) \)

\( \dot{Q}_{ORC, in} \) is the useful heat that is delivered from the heat source to the working fluid in the heater:
\[ \dot{Q}_{ORC, in} = \dot{m}_{HS} (h_{HS, in} - h_{HS, out}) = \dot{m}_{ORC} (h_2 - h_1) \]  
\( (6) \)

In order to evaluate the utilization degree of the heat source, the heat source utilization efficiency \( \eta_{HS,u} \) is defined. The heat source utilization efficiency is equal to the actual heat recovered, \( \dot{Q}_{ORC, in} \), divided by the theoretical maximum amount of heat that could have been recovered from the heat source stream if it was cooled down to the ambient temperature.
\[ \eta_{HS,u} = \frac{\dot{Q}_{ORC, in}}{\dot{m}_{HS} (h_{HS, in} - h_{HS, 0})} \]  
\( (7) \)

Two of the most commonly used performance evaluation parameters of thermodynamic cycles and ORCs are the thermal (or first law/energetic) and exergetic (second law) efficiency. The thermal efficiency of the cycle is used to indicate the percentage of the heat input to the ORC that is converted to electric power:
\[ \eta_{th} = \frac{P_{el}}{\dot{Q}_{ORC, in}} \]  
\( (8) \)

The thermal efficiency is an indicator that takes into account solely the first law of thermodynamics (energy balance), without considering the inherent qualitative difference between heat and mechanical power. In order to include the limitations imposed by the second law of thermodynamics to the conversion of heat to mechanical work in the analysis, the exergy efficiency can be used. The exergy of a thermodynamic system is defined as the theoretical (according to the second law of thermodynamics) maximum work that can be produced if the system is brought into equilibrium with its surroundings. In the case of a heat source consisting of a hot fluid stream, the exergy \( E_{HS} \) of the heat source is given by the expression:
\[ \dot{E}_{HS} = \dot{m}_{HS} \left[ (h_{HS, in} - h_{HS, 0}) - T_0 (s_{HS, in} - s_{HS, 0}) \right] \]  
\( (9) \)

where \( 0 \) refers to the conditions of the environment \((T=15 \, ^\circ C, \, p=1 \, bar)\). The exergy efficiency of the WHR-ORC is expressed as the ratio of the actual work produced by the cycle and the amount of the exergy of the heat source that flows into the system:
\[ \eta_{ex} = \frac{P_e}{\dot{E}_{HS}} \quad (10) \]

From the above equation it can be seen that the exergetic efficiency directly mirrors the net electric power produced by the system. Based on (6) to (10), another expression of the exergetic efficiency can be given by (11):

\[ \eta_{ex} = \eta_{th} \eta_{HS,u} \left[ \frac{(h_{HS,in} - h_{HS,amb})}{(h_{HS,in} - h_h) - T_0 (s_{HS,in} - s_h)} \right] \quad (11) \]

According to the above equation, for any heat source stream of a given quality (enthalpy and entropy), the exergetic efficiency of the WHR-ORC system is the product of two factors. The first one is the thermal efficiency of the ORC, which is intrinsic of the thermophysical properties and the operational points (pressures, temperatures) of the working fluid within the cycle. The second one is the heat source utilization efficiency and reflects the thermal transfer between the working fluid and the heat source fluid stream. The optimization of the exergy efficiency of the cycle is therefore based on the maximization of the value of the product \( \eta_{th} \eta_{HS,u} \). Consequently, both the thermal and heat source utilization efficiency parameters are equally important when designing the WHR-ORC system.

Thermodynamic efficiency optimization (and not necessarily economic) of waste heat recovery schemes is achieved when the net power output (and the concurrent energy savings) is maximized [5]. For this reason, the exergetic efficiency is considered the most suitable performance parameter for the evaluation of such systems, since it indicates the level of utilization of an energy source that would be otherwise left unexploited. However, the maximization of the exergy efficiency does not necessarily lead to optimized cost-competitiveness, since it can involve excessively large heat exchanger surfaces or other equipment (e.g. turbine/pipings) and consequently much higher capital costs that may offset the actual benefits derived from the increased system efficiency. In addition to this, the operating conditions corresponding to the maximum second law efficiency can in some cases be unrealistic, if, for instance, they lead to a very large volume flow ratio in the expander inlet/outlet or extremely high rotational speeds. Nevertheless, the exergy efficiency remains a useful tool for the preliminary assessment of waste heat recovery processes, allowing for coarse level parametric evaluations and screening of working fluid candidates.

Apart from the exergy efficiency, which is used to evaluate the system from a thermodynamic point of view, some other parameters provide more insight into the technical feasibility and economic competitiveness of the WHR-ORC. These are the rotational speed \( n \) (which is in this study calculated assuming a specific turbine speed of 0.1, which is considered as optimal [28]), the Size Parameter \( SP \) of the turbine, the Volume Flow Ratio \( VFR \) of the inlet and outlet streams of the turbine and the UA value (overall heat transfer coefficient \( U \) multiplied by the heat exchange surface \( A \)) in the heater and the condenser. These parameters are described by the following equations:

\[ n = \frac{\Delta h_{exp,ir}^{0.75}}{10 \sqrt[10]{\dot{V}_{exp,out}}} \quad (12) \]

\[ SP = \frac{\dot{V}_{exp,out}}{\Delta h_{exp,ir}^{0.25}} \quad (13) \]

\[ VFR = \frac{\dot{V}_{exp,out}}{\dot{V}_{exp,in}} \quad (14) \]
\[ UA = \frac{\dot{Q}}{\Delta T_{lm}} \]  

In the above equations, \( \Delta h_{\text{exp}, \text{is}} \) is the isentropic specific enthalpy drop in the turbine, \( \dot{V}_{\text{exp, in}} \) and \( \dot{V}_{\text{exp, out}} \) are the volume flow rates of the working fluid at the turbine inlet and outlet respectively, \( \dot{Q} \) is the heat flux of the heat exchanger, and \( \Delta T_{lm} \) is the logarithmic mean temperature difference (LMTD) between the heat exchange fluid streams.

The first three parameters concern the operational applicability of the turbine and are related to its cost. Extremely high rotor speeds may result in unrealistic or costly turbine design (involving expensive magnetic bearings for the turbine shaft), while increased VFR and SP values are associated with larger turbine size and technical complexity. More specifically, the size parameter, introduced by Macchi et al. [29] as a key efficiency optimization parameter for turbines operating with non-conventional fluids, influences the turbine’s actual dimensions (such as blade height). Furthermore, the VFR is inversely correlated with the isentropic efficiency of the expansion. It has been reported that for achieving, for instance, isentropic efficiencies higher than 80%, the VFR value must be lower than 50 [30]. The UA value of a heat exchange process is indicative of the heat transfer equipment required. A high UA value means that more heat needs to be transferred between the heat exchange streams for the desired temperature increase/decrease to be accomplished, with direct implications on the total surface of the heat exchanger and its cost.

### 2.2. Assumptions

#### 2.2.1. Heat source

The thermodynamic simulations are carried out for three heat source inlet temperatures of 150, 225 and 300 °C, representative of low, moderate and high temperature levels of potential waste heat. Since the WHR source is modelled as dry atmospheric air, there are no practical limitations on the minimum temperature of the heat source stream at the heat exchanger outlet (due to condensation or other thermochemical phenomena). In principle this is not the case for waste heat recovery applications. For example, when the heat source stream consists of flue gases or geothermal water, it often cannot be cooled below a certain temperature because of issues such as corrosion of the heat exchange surfaces and other equipment. The characteristics of the heat source stream of the present work are summarized in Table 1.

| Table 1. Heat source characteristics for the application |
|---------------------------------|----------|
| Mass flow | 5 kg/s |
| Temperature | 150, 225, 300 °C |
| Pressure | 2 bar |
| Composition | 78 % N₂, 21 % O₂, 1 % Ar (mole fraction) |

#### 2.2.2. ORC

One of the main parameters of ORC systems is the pinch point of the heat exchangers, which is defined as the minimum temperature difference between the hot and cold fluid streams during the heat exchange in the heater and the condenser. Smaller pinch point values lead to higher heat exchange efficiency, since the amount of heat transferred is higher. On the other hand, due to the limited LMTD between the heat exchange streams, a larger heat exchanger surface is may be required (15). Additional parameters of ORCs include the isentropic efficiency of the pump and the expander. The isentropic efficiencies indicate the deviation of the actual compression/expansion that takes place from the theoretical isentropic process. In the case of the WHR-ORC investigated, they are given by the equations:
\[ \eta_{\text{is,pump}} = \frac{h_1 - h_{4,\text{is}}}{h_1 - h_4} \]  
\[ \eta_{\text{is,exp}} = \frac{h_2 - h_3}{h_2 - h_{3,\text{is}}} \]  

The maximum operation pressure of the ORC (which is the pressure under which the heating of the working medium takes place) is varied within a specified range and the cycle’s evaluation parameters which were introduced in the Section 2.2 are estimated. Under the subcritical ORC, the maximum value of the operation pressure is set to 90% of the critical pressure \( p_{\text{crit}} \) of the working fluid. In the case of the supercritical ORC, the pressure is varied from 103 to 130% of \( p_{\text{crit}} \). These limitations on the pressure range of the system are based on two reasons. Firstly, it has been shown that near the critical point of the working fluid its thermophysical properties become unstable [22, 31]. Secondly, an upper limit to the maximum operating pressure of the ORC is posed in order to maintain realistic pressure ratio values and avoid overly costly equipment. In the supercritical ORC, the turbine inlet temperature of the working fluid is set to 20 K above its critical temperature, in order to ensure that there is no liquid phase formed during its expansion.

The assumptions followed for the simulations are summarized in Table 2.

**Table 2. ORC simulation parameters**

<table>
<thead>
<tr>
<th>Efficiencies</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expander isentropic efficiency (( \eta_{\text{is,pump}} ))</td>
<td>75%</td>
</tr>
<tr>
<td>Pump isentropic efficiency (( \eta_{\text{is,pump}} ))</td>
<td>80%</td>
</tr>
<tr>
<td>Electromechanical efficiency (( \eta_{\text{m}} \eta_{G} ))</td>
<td>95%</td>
</tr>
<tr>
<td>Pump motor efficiency (( \eta_{M} ))</td>
<td>85%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Heat exchangers</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pinch point heater</td>
<td>35 K</td>
</tr>
<tr>
<td>Pinch point condenser</td>
<td>10 K</td>
</tr>
<tr>
<td>Cooling water inlet temperature</td>
<td>20 °C</td>
</tr>
<tr>
<td>Cooling water temperature increase</td>
<td>15 K</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Operating pressures</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum subcritical pressure</td>
<td>90% of ( p_{\text{crit}} )</td>
</tr>
<tr>
<td>Maximum supercritical pressure</td>
<td>130% of ( p_{\text{crit}} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Operating temperatures</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum subcritical ORC temperature</td>
<td>Saturation temperature at operating pressure</td>
</tr>
<tr>
<td>Maximum supercritical ORC temperature</td>
<td>( T_{\text{crit}} +20 ) K</td>
</tr>
</tbody>
</table>

Depending on the heat source temperature, the pinch point limitation in the heater cannot not be met for the whole range of operating pressures. In other instances (for Propane), the turbine outlet stream of the working fluid is in the dual phase region of the T-s diagram. In all of the above cases, the results are rejected and as unacceptable. This is because the pinch point limitation is essential in order to maintain a fair comparison between the working fluids and their operational points. At the same time, since at the power ranges investigated in the present work the expander is of the turbine type, the condensation of the working medium during the expansion process is undesirable.

### 2.3. Working fluids

#### 2.3.1. Pure fluids

The set of the examined pure working fluids and their critical temperatures and pressures is given in Table 3. Additional information given is the Ozone Depletion Potential (ODP), the Global Warming Potential (GWP) and the ASHRAE Safety Group for each fluid [32]. The working fluids
investigated include the natural refrigerants butane, cyclopentane, hexane, pentane and propane, along with R245fa, which is used as benchmark fluid. Heptane, Octane etc. are not examined due to their significantly higher critical temperature, which results in their low efficiency for the heat source temperatures considered (as will be shown later). Methane was excluded from the study because of its extremely low critical temperature (-83.59 °C) which results in an entirely different cycle configuration (the condensation is replaced by supercritical cooling). Methanol, on the other hand, has a critical pressure which is too high (81 bar), so for a condensation temperature of around 40 °C (at 0.36 bar) the system would operate in technically unrealistic pressure ratios. The reasons for the selection of R245fa regard its reported favourable environmental properties and good thermodynamic performance in low/mid temperature ORC applications [3, 5, 13].

Table 3. Properties of the pure organic fluids that are examined

<table>
<thead>
<tr>
<th>Fluid</th>
<th>$p_{\text{crit}}$ (bar)</th>
<th>$T_{\text{crit}}$ (°C)</th>
<th>ODP</th>
<th>GWP</th>
<th>ASHRAE Safety Group</th>
<th>Molecular weight (kg/kmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butane</td>
<td>37.96</td>
<td>151.98</td>
<td>0</td>
<td>4</td>
<td>A3</td>
<td>58.1</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>45.15</td>
<td>238.54</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>70.1</td>
</tr>
<tr>
<td>Hexane</td>
<td>30.34</td>
<td>234.67</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>86.2</td>
</tr>
<tr>
<td>Pentane</td>
<td>33.7</td>
<td>196.55</td>
<td>0</td>
<td>4±2</td>
<td>A3</td>
<td>72.1</td>
</tr>
<tr>
<td>Propane</td>
<td>42.51</td>
<td>96.74</td>
<td>&lt;0</td>
<td>3.3</td>
<td>A3</td>
<td>44.1</td>
</tr>
<tr>
<td>R245fa</td>
<td>36.51</td>
<td>154.01</td>
<td>0</td>
<td>950</td>
<td>A1</td>
<td>134.1</td>
</tr>
</tbody>
</table>

The energetic efficiency for the pure fluids as a function of the maximum operation pressure of the ORC is plotted in Fig. 2. The second part of each curve corresponds to the supercritical pressure range. It can be seen that for all fluids the thermal efficiency increases for higher pressures while the supercritical ORC results in a higher thermal efficiency for all the refrigerants. It should be noted, though, that the thermal efficiency increase rate is much higher in the lower pressure range. For higher supercritical pressures, the energetic efficiency tends to gradually converge to a relatively steady value.

![Fig. 2. Energetic efficiency of the natural refrigerants examined](image)

A strong positive correlation between the critical temperature of each fluid and its thermal efficiency can also be observed. As a matter of fact, Propane, with a critical temperature of 96.74 °C, has the lowest thermal efficiency and Cyclopentane, with a much higher critical temperature (238.54 °C), has the highest. The link between the working fluid’s critical temperature and its overall thermal efficiency can be explained by the fact that, for fluids of higher critical temperatures, the turbine inlet temperature at a given pressure is generally at a higher level than for fluids of lower critical temperatures. This is due to the assumptions followed in the present work.
(no superheating for subcritical cycle/maximum temperature 20 K above $T_{crit}$ for supercritical cycle). Given a fixed condensation temperature, the thermal efficiency is increased as the average temperature of the heat input to the working fluids increases. This can be also seen from Fig. 3:

![Fig. 3. Rankine cycle thermal efficiency for increasing evaporation temperatures](image)

As the evaporation temperature rises, the area $E_h$ that is below the curve $1\rightarrow2$ ($1\rightarrow2'$) increases at a higher rate than the area $E_c$ that is below the curve $3\rightarrow4$ ($3'\rightarrow4$). Consequently, the thermal efficiency of the cycle increases.

### 2.3.2. Binary zeotropic mixtures

The natural pure working fluids that are presented in Table 3 can produce 10 possible binary mixture combinations, summarized in Table 4. The relative molar concentration of the components of each mixture adds several additional cases to the problem of the zeotropic mixtures selection and their respective composition. For supercritical conditions, a number of mixtures are excluded based on their critical temperature, given the pinch point limitation in the evaporator. As a first approach for the thermodynamic evaluation, it was decided to set every mixture component ratio to 50 %. However, it must be noted that eventually the efficiency of the fluid mixtures may be maximized at varying ratios [23, 25]. Consequently, further sensitivity analysis on the effect of the fluid composition on the system efficiency is carried out for the mixtures that have the highest efficiency at 50/50 ratio in each case, in order to find the optimal value of this parameter.

The above assumptions suggest that the aim of the current work is the preliminary investigation and presentation of the efficiency potential of some indicative natural refrigerants and their mixtures and not the complete optimization of the WHR-ORC.

<table>
<thead>
<tr>
<th>Table 4. Properties of binary mixtures at 50/50 molar concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>p_{crit}</strong> (bar)</td>
</tr>
<tr>
<td>----------------------</td>
</tr>
<tr>
<td>Butane-Cyclopentane</td>
</tr>
<tr>
<td>Butane-Hexane</td>
</tr>
<tr>
<td>Butane-Pentane</td>
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<tr>
<td>Butane-Propane</td>
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<td>Cyclopentane-Hexane</td>
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<td>Cyclopentane-Pentane</td>
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<td>Cyclopentane-Propane</td>
</tr>
<tr>
<td>Hexane-Pentane</td>
</tr>
<tr>
<td>Hexane-Propane</td>
</tr>
<tr>
<td>Pentane-Propane</td>
</tr>
</tbody>
</table>
In Fig. 4 the thermal efficiency of the binary mixtures of Table 4 is plotted against the maximum operation pressure of the ORC. Similarly to the case of pure fluids, there is a positive correlation between the thermal efficiency of the working fluid, the operation pressure and its critical temperature. Cyclopentane/Hexane and Cyclopentane/Pentane (with critical temperatures 236.50 °C and 217.55 °C respectively) have the highest thermal efficiencies while Pentane/Propane ($T_{crit}=146.62$ °C), Hexane/Propane ($T_{crit}=165.57$ °C) and Butane/Propane ($T_{crit}=124.33$ °C) have the lowest thermal efficiencies.

### 3. Results and discussion

The results of the simulations are organized in the following manner: for each heat source temperature, the exergy efficiency is plotted as a function of the operation pressure for a) pure fluids, b) binary fluid mixtures for subcritical and supercritical conditions. The pure fluids and the binary mixtures exhibiting the maximum exergy efficiency for subcritical and supercritical operating pressures are identified and their performance evaluation and other technical operation parameters are calculated and discussed.

#### 3.1. Heat source temperature of 150 °C

Due to the relatively low heat source temperature, the minimum pinch point requirement in the heater is not met for supercritical pressures for any of the pure fluids/mixtures examined, since their critical temperatures are substantially high. Therefore, the results shown refer only to the subcritical pressure range. The mixture of Hexane/Propane has a very small operating range between 5-7 bar with a low exergy efficiency (2-4%), so it is unnecessary to plot these results along with the other mixtures.
Fig 5. Exergy efficiency a) pure fluids and b) binary zeotropic mixtures at a heat source temperature of 150 °C

3.1.1. Pure fluids- \( T_{HS,in}=150°C \)

As can be observed in Fig. 5, for all the pure fluids and mixtures except for Propane, there is an optimal evaporation pressure that maximizes the exergy efficiency. This can be attributed to two antagonistic effects that take place while the operation pressure increases. On one hand, due to the constant pinch point assumption in the heater, as the turbine inlet temperature of the working fluid increases (because the working medium enters the expander as saturated vapor), so does the outlet temperature of the heat source stream. As a result, the heat absorbed by the working fluid \( \dot{Q}_{ORC,in} \) (which is essentially the heat input to the ORC) is decreased. In other words the value of \( \eta_{HS,u} \) is diminished. This effect (effect 1) has a detrimental impact on the second law efficiency of the system.

On the other hand, increasing the evaporation pressure leads to an increase in the thermal efficiency \( \eta_{th} \) of the cycle (effect 2). This is because the specific work produced by the turbine increases at a higher rate than the specific work consumed by the pump as the pressure ratio gets higher. Up to a certain evaporation pressure, the negative effect of the decreasing heat input to the ORC (effect 1) is counter balanced by the positive effect of the energy efficiency increase (effect 2). However, after a certain value of the evaporation pressure, which largely depends on the thermophysical properties of the working fluid, the specific work of the turbine and subsequently the cycle’s thermal...
efficiency increase at a continuously lower rate (as seen in Fig. 2). The optimal evaporation pressure corresponds to the pressure beyond which the benefits of the increasing thermal efficiency (effect 2) cannot compensate for the decreasing heat input (effect 1) that is supplied to the ORC. At this point the value of $\eta_{\text{HS,u}}$ is maximized before starting to decline.

The efficiency curve of Propane is an exception to the above pattern. Its exergetic efficiency curve increases monotonously with increasing the maximum operating pressure. The reason for this difference is the fluids’ significantly lower critical temperature, which results in smaller evaporation temperatures. Given the constant pinch point assumption, it is thus possible to better make use of the heat content of the heat source over a larger pressure range by cooling it to even lower temperatures. The decrease rate of $\eta_{\text{HS,u}}$ is hence lower as the pressure increases, compared to the other pure fluids.

The described effect can be seen in more detail in Fig. 6, where the heat source utilization efficiency of Propane ($T_{\text{crit}}=96.74$ °C), Butane ($T_{\text{crit}}=151.98$ °C) and Cyclopentane ($T_{\text{crit}}=238.54$ °C) for heat source temperatures of 150, 225 and 300°C are plotted as a function of the maximum operation cycle pressure. It can be seen that for the lower heat source temperatures (150 and 225 °C) the high critical temperature fluids have a significantly lower $\eta_{\text{HS,u}}$ which rapidly decreases as the evaporation pressure (and temperature) increases. When the heat source temperature is sufficiently high (300 °C), the heat source utilization efficiency is much higher, and its rate of its decrease as the evaporation temperature of the working fluids becomes higher is less significant.

The dependence of the first law and heat source utilization efficiency on the critical temperature of the fluids can also help explain why for the heat source temperature of 150 °C, high critical temperature working fluids tend to perform better in the lower pressure range (before their heat source utilization efficiency dramatically diminishes). The importance of the heat source utilization efficiency can be stressed by the fact that despite propane exhibiting the lowest energetic efficiency, its exergy efficiency, which is the primary evaluation parameter of the WHR-ORC system, is significantly higher than in the case of the other pure fluids.

**3.1.2. Binary zeotropic mixtures - $T_{\text{HS,in}}=150^\circ\text{C}$**

When using zeotropic mixtures, the exergetic efficiency is mainly affected by two effects. The first concerns the temperature glide of the working fluid during its evaporation (in subcritical cycles) and its condensation. Depending on the concentration of the mixture components, the temperature glide can help improve the matching of the temperatures between the heat source (heater), cooling medium (condenser) and the working fluid. This can in turn lead to reduced irreversibility and exergy losses during the heat exchange processes of the WHR-ORC system.

![Fig. 6. Heat source utilization efficiency as a function of the maximum operation pressure for heat source temperatures of 150, 225 and 300 °C for Propane, Butane and Cyclopentane](image-url)
This effect is illustrated in Fig. 7. The area enclosed by the Q-T lines of the heat source and the working fluid (evaporator) and cooling medium and working fluid (evaporator) is equal to the irreversibility $I$ of the heat exchange:

$$\int (T_h - T_c) d\dot{Q} = \int T_h d\dot{Q} - \int T_c d\dot{Q} = \int d\dot{E}_h - \int d\dot{E}_c = \Delta \dot{E}_h - \Delta \dot{E}_c = I$$

In the above equation, 1 stands for one side and 2 for the other side of the heat exchanger. It is evident that the exergy losses are minimized when the temperature profiles of the hot and cold stream are perfectly matched. For a fixed pinch point value, this happens when they are almost parallel to each other, minimizing the area between them. The absolute difference $|\Delta T_h - \Delta T_c|$ can be used as an indicator of the matching between the temperatures of the hot and cold stream during the phase change of either. As $|\Delta T_h - \Delta T_c|$ approaches zero, the Q-T lines tend to have the same slope and the exergy destruction decreases. On the other hand, the higher the $|\Delta T_h - \Delta T_c|$ value, the higher the irreversibility of the heat exchange.

It has been previously stated [23, 24] that because the temperature glide in the condenser is usually higher than the glide in the evaporator, the overall exergy efficiency can be mostly improved when the exergy destruction losses in the condenser are minimized. An emphasis has been consequently given on the matching of the temperature profiles in the condenser (indicated by $|\Delta T_{cw} - \Delta T_{glide}|$), as a criterion for optimizing the cycle.

The second parameter that determines the exergetic efficiency of zeotropic fluid mixtures is their critical temperature (and thus evaporation temperature range) compared to their parent components, which greatly influences the heat source utilization efficiency as well as the thermal efficiency of the WHR-ORC (Section 3.1.1.) especially in lower heat source temperatures.

Similarly to the case of pure working fluids, for the heat source temperature of 150 °C the impact of the critical temperature is dominant in determining the exergetic efficiency of the cycle. It is therefore no surprise that the mixture with the smallest critical temperature (Butane/Propane) has also the biggest second law efficiency, despite its energetic efficiency being among the lowest ones. It is also notable that higher second law efficiencies are attainable by using mixtures of Butane/Cyclopentane, Butane/Hexane, Butane/Pentane, and Hexane/Pentane than by using their
pure most efficient pure components. On the other hand, the mixtures of Propane with other fluids at 50/50 concentrations do not exhibit higher exergetic efficiency than pure Propane.

A sensitivity analysis on the effect of the composition of the Propane/Butane and Butane/Cyclopentane mixtures is carried out in order to explore its effect on the performance of the system. These two mixtures are selected for the analysis because they exhibit the highest maximum exergy efficiency at 50/50 concentration. The composition of the mixtures is varied in steps of 10 %. For each step, the optimum (with respect to the exergy efficiency) operation pressure is identified. The values of the $\eta_{\text{ex}}$, $\eta_{\text{th}}$, $\eta_{\text{HS,u}}$ and the absolute difference between the temperature glide of the mixture and the temperature increase of the cooling medium during the condensation of the former $|\Delta T_{cw}-\Delta T_{\text{glide}}|$ are plotted in Fig. 8.

![Graphs showing the effect of concentration on efficiency and temperature glide](image)

**Fig. 8** The effect of the relative concentration of the mixtures a) Butane/Propane and b) Butane/Cyclopentane on the system efficiency indicators and the matching of the temperatures of the working fluid and cooling medium in the condenser. For each value of the concentration, the characteristics of the optimal operational pressure are plotted.

The temperature glide of the fluid mixtures in the condenser depends on the relative concentration of their components and the condensation pressure/temperature. Its variation when changing the maximum operation pressure of the ORC is negligible. In the case of pure fluids, $\Delta T_{\text{glide}}$ is zero, which is indicated by the maxima of the $|\Delta T_{cw}-\Delta T_{\text{glide}}|$ in the values of 0 and 100 % of the x axis. In this case, $|\Delta T_{cw}-\Delta T_{\text{glide}}| = \Delta T_{cw}$ which is the temperature difference of the cooling water during the phase change of the pure fluids. $\Delta T_{\text{glide}}$ increases for intermediate values of the concentration ratio of the binary mixture components. A third maximum of the $|\Delta T_{cw}-\Delta T_{\text{glide}}|$ value (as in the case of Butane/Cyclopentane) may occur if the temperature glide of the mixture surpasses the value of $\Delta T_{cw}$. In this case, two local minima of the $|\Delta T_{cw}-\Delta T_{\text{glide}}|$ occur for two intermediate concentration values as the temperature glide approaches the $\Delta T_{cw}$. Depending on the temperature glide variation of each mixture and the temperature increase of the coolant stream in the condenser (set at 15 K in the present study), there may be one or two minima of $|\Delta T_{cw}-\Delta T_{\text{glide}}|$.

These two patterns of the $|\Delta T_{cw}-\Delta T_{\text{glide}}|$ curves are common for all instances of the binary mixtures that are examined in the present study. It should be stressed, nevertheless, that the concentration values that correspond to the $\Delta T_{\text{glide}}$ maximum are not necessarily the same for all binary mixtures. For example, it has been shown that for the mixture of Pentane/R245fa the temperature glide is maximized for a ratio of around 75/25 [25]. In the case of Butane/Propane (Fig 8 (a)), the temperature glide has its highest value in a component ratio of 50/50.
For the specific binary mixtures that are examined, Butane10/Propane90 exhibits the highest exergetic efficiency (23.20%) which is higher than the efficiency of pure Propane (21.02 %) by around 10%. In the case of Butane/Cyclopentane, the concentration 70/30 is the optimal, with an exergy efficiency of 16.50 %, 23.47% higher than Butane. In the case of Butane/Propane, due to the significantly low critical temperature of Propane, the maximum of the exergy efficiency occurs for a high Propane concentration and the effect of the temperature glide on the efficiency has a minor influence. For Butane/Cyclopentane (Fig. 8 (b)), though, which both have higher critical temperatures, the second law efficiency is optimized when the $|\Delta T_{cw} - \Delta T_{glide}|$ is minimized and the concentration of Butane (which has the lower critical temperature) is higher. It should also be noted that a second local maximum of the exergetic efficiency occurs near the second minimum of the $|\Delta T_{cw} - \Delta T_{glide}|$ difference (Butane20/Cyclopentane80).

From the above observations it can be stated that when the heat source temperature is 150 °C the exergy efficiency of the fluid mixtures, is affected by the combined effect of their critical temperature and temperature matching in the condenser.

### 3.1.3. Overview $T_{HS,\text{in}}=150^\circ\text{C}$

In Table 5 the cases of the working fluids that exhibit the best second law efficiency are summarized. Both Propane and the Propane/Butane mixture have higher optimal exergetic efficiency than R245fa (approximately by 70-80 %), as well as higher thermal and heat source utilization efficiencies. All three fluids operate under similar pressure ratios (2.59 to 2.90). However, the maximum operation pressure of R245fa is much lower (~1/8) compared to the other working fluids. The UA values of the heater and condenser for all three cases have a minor difference, being slightly lower for R245fa. Although R245fa has a low VFR and rotational speed, its turbine SP and volume flowrate at turbine outlet are significantly higher. Considering the above, from a thermodynamic and technical/economic standpoint, it seems that Propane/Butane and also Propane could be attractive alternatives to R245fa for the utilization of heat sources of 150 °C. A matter that has to be yet to resolved, nevertheless, involves the safety concerns of using Propane as a working fluid for WHR-ORCs, given its high flammability.

#### Table 5. Operational characteristics of optimal fluids at 150 °C heat source temperature

<table>
<thead>
<tr>
<th>Working fluid</th>
<th>Pure working fluids</th>
<th>Binary fluid mixtures</th>
<th>R245fa (Subcritical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (bar)</td>
<td>38.23</td>
<td>37.26</td>
<td>8.10</td>
</tr>
<tr>
<td>$\eta_{ex}$ (%)</td>
<td>21.02</td>
<td>23.20</td>
<td>13.04</td>
</tr>
<tr>
<td>$\eta_{th}$ (%)</td>
<td>10.74</td>
<td>11.19</td>
<td>7.03</td>
</tr>
<tr>
<td>$\eta_{HS,u}$ (%)</td>
<td>35.25</td>
<td>37.34</td>
<td>33.39</td>
</tr>
<tr>
<td>$T_{\text{max}}$ (°C)</td>
<td>110.65</td>
<td>96.51</td>
<td>81.37</td>
</tr>
<tr>
<td>Pressure ratio</td>
<td>2.59</td>
<td>2.90</td>
<td>2.85</td>
</tr>
<tr>
<td>$P_{\text{el}}$ (kW)</td>
<td>25.85</td>
<td>28.53</td>
<td>16.04</td>
</tr>
<tr>
<td>$UA_{\text{heat}}$ (kWth/K)</td>
<td>5.72</td>
<td>6.07</td>
<td>4.67</td>
</tr>
<tr>
<td>$UA_{\text{cond}}$ (kWth/K)</td>
<td>14.02</td>
<td>16.40</td>
<td>13.33</td>
</tr>
<tr>
<td>$V_{\text{exp,out}}$ (m³/h)</td>
<td>27.63</td>
<td>95.24</td>
<td>268.08</td>
</tr>
<tr>
<td>$n$ (RPM)</td>
<td>19834</td>
<td>16691</td>
<td>5780</td>
</tr>
<tr>
<td>SP (m)</td>
<td>0.010</td>
<td>0.011</td>
<td>0.023</td>
</tr>
<tr>
<td>VFR</td>
<td>2.94</td>
<td>3.91</td>
<td>3.00</td>
</tr>
</tbody>
</table>

### 3.2. Heat source temperature of 225 °C

When the heat source stream inlet temperature is 225 °C, there is the possibility to consider supercritical pure fluids and binary mixtures as options for the WHR-ORC.
Fig. 9 Exergy efficiency a) pure fluids and b)binary zeotropic mixtures at a heat source temperature of 225°C

3.2.1. Pure fluids-T_{HS,in}=225°C

The pattern of the “bell” shaped $\eta_{ex}$-$p$ curves appears also in this heat source temperature (Fig. 9). However both R245fa and Butane now follow the exception of Propane, whose second law efficiency increases monotonously with the maximum operating pressure. Based on the detailed discussion of Section 3.1.1, this behavior can be interpreted by these fluids’ low critical temperatures, permitting a higher $\eta_{HS,u}$ value for increasing pressures (and first law efficiency). The positive relation between the exergetic efficiency and the turbine inlet pressure for Butane, Propane and R245fa can be observed in both the subcritical and the supercritical operating range. Nevertheless, an abrupt efficiency drop can be noticed in the beginning of the supercritical region for Butane and R245fa. This drop can be justified by the non-continuous increase of the turbine inlet temperature (20 K above $T_{crit}$) which is assumed in supercritical conditions. In the case of Propane, a superheating of 20 K was already assumed under subcritical temperatures (because it is a wet fluid), so the transition point of the exergy efficiency curve is smoother.

Among the pure fluids, Butane exhibits the highest optimal exergy efficiency in both subcritical and supercritical pressures (39.16% and 42.49 % respectively), closely matching the efficiency of
R245fa. In the lower pressure range (below 12 bar), Pentane has the highest exergetic efficiency (27.74%), while below 5 bar hexane exhibits the best performance (around 25%). The reason behind Butane’s advantageous overall performance compared to the other fluids is the moderate difference between the temperature of the heat source and its critical temperature. As a result, the operation of the working fluid under an increased pressure ratio (and energetic efficiency) does not hinder the utilization of the heat source.

3.2.2. Binary zeotropic mixtures - $T_{HS,in}=225^\circ$C

Similarly to the case of pure fluids, for the binary mixtures which have high critical temperatures (such as Cyclopentane/Hexane, Cyclopentane/Pentane, and Hexane/Pentane) there exists an optimal maximum operation pressure where the exergetic efficiency is maximized. On the other hand, for mixtures with critical temperatures below 165 °C the efficiency increases monotonously with the pressure. Butane/Propane has the maximum second law efficiency (38.99% subcritical and 46.18 % supercritical). At moderate pressure ranges below 25 bar the efficiency of Butane/Pentane is the highest among the fluid mixtures, taking values around 30-32%. In lower pressures the mixture of Hexane/Pentane presents the optimal efficiency (27.96 %). Similarly to the case of the pure refrigerants, working fluids with low critical temperatures tend to perform better in high pressures. High critical temperature fluids, on the other hand, are more competitive in lower pressures and are distinguished by the bell shaped $\eta$-pressure curve.

A sensitivity analysis on the composition of the Butane/Propane mixture under subcritical (Fig. 10 (a)) and supercritical (Fig. 10 (b)) conditions follows in order to determine its impact on the performance of the working fluid.

![Graph](image)

(a)  
(b)

*Fig. 10 The effect of the relative concentration of the components of the mixture Butane/Propane under a) subcritical and b) supercritical maximum operating pressures on the system efficiency indicators and the matching of the temperatures of the working fluid and cooling medium in the condenser. For each value of the concentration, the characteristics of the optimal operational pressure are plotted.*

The mixtures Butane70/Propane30 (subcritical ORC) and Butane60/Propane40 (supercritical ORC) exhibit the highest exergy efficiency. Compared to pure Butane, the first second law efficiency improvement is equal 2.58 and 8.88 % respectively. The difference $\Delta T_{cw}-\Delta T_{glide}$ is 3.14 K in the first case and 2.28 K in the second. A tendency of the exergy efficiency to reach its maximum value near the local minimum of the value of $\Delta T_{cw}-\Delta T_{glide}$ that is achieved when the concentration of the most efficient pure component (i.e. Butane) is dominant can be again identified.
3.2.3. Overview - \( T_{HS,in} = 225^\circ C \)

As can be seen in Table 6, compared to R245fa, pure butane has higher exergetic efficiency under both subcritical and supercritical conditions by around 4.30 \%. Although its rotational speed is as much as double, it has a substantially decreased \( \dot{V}_{exp,\text{out}} \), SP and VFR, with equivalent UA values and a lower pressure ratio. Consequently, its superiority as a working fluid when the heat source temperature is at 225 \(^\circ C\) is not only limited to its thermodynamic performance but also concerns technical aspects of its use as a working fluid.

By replacing pure Butane with a mixtures of Propane70/Butane30 (subcritical) and Butane40/Propane60 (supercritical), the exergy efficiency can be improved by 2.58 \% and 8.82 \%. Under subcritical operation, the pressure ratio, SP, VFR and \( \dot{V}_{exp,\text{out}} \) are lower for Butane30/Propane70. However, the UA value in the condenser is substantially higher. This is because of the reduced \( \Delta T_{\text{lm}} \) due to the temperature glide during the phase change of the mixture. As a result, although in terms of turbine operation the use of the fluid mixture is favorable, it may require more rigorous condenser design, with subsequent reverberations on the heat exchanger costs.

The above remarks also apply when considering the supercritical WHR-ORC comparing pure Butane and Butane40/Propane60. However, in this case, the potential benefits in the exergy efficiency are greater compared to the case of the subcritical ORC and the use of the fluid mixture becomes more attractive.

The supercritical ORC generally results in improved exergetic system efficiency (by around 9 \% and 5 \% in the case of in the case of Butane and R245fa respectively), increased pressure ratios, rotational speeds and VFR values in the turbine, while the volume flow ratio at the expander outlet and size parameter are lower compared to the subcritical cycle.

To sum up, when the heat source temperature is 225\(^\circ C\), the use of Butane and Butane/Propane mixtures as replacements of R245fa has considerable benefits from both thermodynamic and technical aspects.

| Table 6. Operational characteristics of optimal fluids at 225 \(^\circ C\) heat source temperature |
|--------------------------------------------------|--|--------------------------------------------------|--|--------------------------------------------------|--|--------------------------------------------------|--|--------------------------------------------------|
| Working fluid | Pure working fluids | Binary mixture fluids | R245fa |
| | a) Sub | b) Super | a) Sub | b) Super | a) Sub | b) Super |
| Pressure (bar) | 34.16 | 49.35 | 35.38 | 51.70 | 32.76 | 47.32 |
| \( \eta_{ex} \) (%) | 39.16 | 42.65 | 40.17 | 46.41 | 38.28 | 40.29 |
| \( \eta_{th} \) (%) | 14.92 | 17.14 | 13.81 | 15.92 | 14.60 | 16.50 |
| \( \eta_{HS,u} \) (%) | 65.50 | 62.12 | 72.60 | 72.75 | 65.43 | 60.95 |
| \( T_{\text{max}} \) (\(^\circ C\)) | 145.28 | 171.97 | 131.22 | 149.85 | 148.06 | 174.05 |
| Pressure ratio | 8.19 | 11.95 | 6.42 | 8.35 | 11.72 | 17.24 |
| \( P_{el} \) (kW) | 104.24 | 113.53 | 106.93 | 123.54 | 101.91 | 107.26 |
| \( UA_{\text{heat}} \) (kW/\text{K}) | 16.78 | 16.75 | 17.37 | 17.94 | 16.98 | 16.27 |
| \( UA_{\text{cond}} \) (kW/\text{K}) | 38.34 | 35.95 | 55.70 | 58.86 | 38.15 | 35.01 |
| \( \dot{V}_{exp,\text{out}} \) (\( \text{m}^3/\text{h} \)) | 611.85 | 576.39 | 527.96 | 479.44 | 773.82 | 717.79 |
| \( n \) (RPM) | 11035 | 12621 | 11016 | 12048 | 6057 | 7003 |
| SP (m) | 0.025 | 0.023 | 0.023 | 0.022 | 0.032 | 0.030 |
3.3. Heat source temperature of 300 °C

Fig. 11 Exergy efficiency a) pure fluids and b) binary zeotropic mixtures at a heat source temperature of 300 °C

3.3.1. Pure fluids-\(T_{\text{HS,in}}=300^\circ\text{C}\)

Due to the high value of the heat source temperature the decrease of the \(\eta_{\text{HS,u}}\) as the turbine inlet temperature rises is relatively smaller than in the previous cases (Sections 3.1 and 3.2) examined. At the same time, the positive effect of the enhancement of the energetic efficiency of the working fluids for increasing maximum operating pressures remains unaffected. The overall result is the disappearance of the bell shaped \(\eta_{\text{ex}-p}\) curves (Fig. 11). Consequently, for all the pure fluids and binary mixtures, the exergetic efficiency of the WHR-ORC rises monotonously with increasing pressure and is maximized when the latter takes its highest value. The initial decrease of the \(\eta_{\text{ex}}\) at the lower range of the supercritical operating pressures can be again attributed to the non continuous increase of the maximum operating temperature of the ORC.

Under both subcritical and supercritical conditions, Pentane exhibits the highest exergetic efficiency (43.17 and 46.49% respectively). Nevertheless, for evaporating pressures below 25 bar, hexane has a consistently higher efficiency of around 40%. This is in accordance with the relation between the
optimal operation pressure range for each fluid and its critical temperature which was described previously.

3.3.2. Binary zeotropic mixtures- $T_{HS,\text{in}}=300^\circ\text{C}$

Although for pressures below 27 bar the mixtures of Hexane/Pentane and Cyclopentane/Hexane have the best performance, Butane/Cyclopentane exhibits the highest overall exergetic efficiency (45.96 %) at 37.38 bar for subcritical conditions. The same working fluid has the highest second law efficiency under supercritical pressures ($\eta_{ex}=49.87$% at 53.99 bar). The potential of improving the exergetic efficiency by varying the composition of the fluid mixture is illustrated in Figure 12 where a sensitivity analysis is carried out for subcritical and supercritical cycle configuration.

![Figure 12](image_url)

*Fig. 12 The effect of the relative concentration of the components of the mixture Butane/Cyclopentane under (a) subcritical and (b) supercritical maximum operating pressures on the system efficiency indicators and the matching of the temperatures of the working fluid and cooling medium in the condenser. For each value of the concentration, the characteristics of the optimal operational pressure are plotted.*

Under subcritical conditions, the mixture Butane30/Cyclopentane70 has the highest exergetic efficiency (46.17 %). Butane50/Cyclopentane50 has the best performance in supercritical operation pressures. The exergy efficiency improvement that is achieved by the use of the binary mixtures instead of their most efficient pure component is equal to 13.54 % (subcritical) and 16.34 % (supercritical). The exergy efficiency is closely connected to the matching of the temperature profiles of the working fluid and the cooling water in the condenser, since the local exergy efficiency maxima coincide with the minimization of the $|\Delta T_{cw}-\Delta T_{glide}|$ value.

3.3.3. Overview- $T_{HS,\text{in}}=300^\circ\text{C}$

In the case of the heat source stream inlet temperature being 300 °C, Pentane is the best pure fluid for the WHR-ORC. In subcritical conditions, it has an exergetic efficiency of 43.17%, which is 17.44% higher than the efficiency of R245fa. An efficiency increase of 7.69% can be attained when the cycle operates in supercritical pressures. Compared to supercritical R245fa, Pentane’s second law efficiency is 12.11% higher. Nonetheless, R245fa operates under a substantially lower pressure ratio and VFR (roughly half). Meanwhile, the volume flow rate of the working fluid at the turbine outlet is significantly lower at about 50% in subcritical and supercritical conditions. At the same time, it has much more favourable UA values in the evaporator and the condenser while it has a
smaller SP and rotational speed. The above considerations suggest that although from a purely thermodynamic standpoint Pentane is a better candidate for the WHR-ORC than R245fa, its use may be associated with higher costs due to the more challenging design of the turbine and increased heat exchanger surface.

The performance of the subcritical ORC can be further improved by substituting Pentane with a mixture of Butane30/Cyclopentane70. The result is a 6.95% increase in the exergy efficiency. Additionally, there is a slight decrease in the SP and the $\dot{V}_{\text{exp, out}}$. However, the pressure ratio, rotational speed, VFR and UA values of the evaporator and the condenser are higher. The supercritical WHR-ORC of Butane50/Cyclopentane50 leads to a further increase in the exergy efficiency by 6.82%. Compared to the supercritical R245fa, this accounts to an improvement of 18.93%. Besides the beneficial effect on the exergy efficiency, the operation of the cycle with the Butane/Cyclopentane mixture results in a decrease of $\dot{V}_{\text{exp, out}}$ by about 25% as well as a slight decrease in the size parameter of the turbine. The main drawbacks include the increase of the UA value of the condenser and the rotational speed of the turbine by approximately 10%. However, the overall advantageous values of the technical evaluation parameters of R245fa under supercritical conditions do not allow to ultimately identify the Butane50/Cyclopentane50 mixture as the optimal working fluid.

Similarly to the case of $T_{\text{HS}}=225^\circ\text{C}$, the supercritical cycle is generally associated with higher pressure ratios, rotational speeds and VFRs, while tending to have a somewhat decreased $\dot{V}_{\text{exp, out}}$ and SP.

**Table 7. Operational characteristics of optimal fluids at 300 °C heat source temperature**

<table>
<thead>
<tr>
<th>Working fluid</th>
<th>Pure working fluids</th>
<th>Binary mixture fluids</th>
<th>R245fa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (bar)</td>
<td>Pentane 30.33</td>
<td>Pentane (30/70) 38.66</td>
<td>Butane/Cyclopentane (50/50) 52.39</td>
</tr>
<tr>
<td>$\eta_{\text{ex}}$ (%)</td>
<td>43.17</td>
<td>46.17</td>
<td>49.32</td>
</tr>
<tr>
<td>$\eta_{\text{th}}$ (%)</td>
<td>17.02</td>
<td>18.58</td>
<td>19.09</td>
</tr>
<tr>
<td>$\eta_{\text{HS,u}}$ (%)</td>
<td>77.67</td>
<td>76.06</td>
<td>79.10</td>
</tr>
<tr>
<td>$T_{\text{max}}$ (°C)</td>
<td>189.42</td>
<td>206.36</td>
<td>215.26</td>
</tr>
<tr>
<td>Pressure ratio</td>
<td>Pentane 25.12</td>
<td>Butane/Cyclopentane (30/70) 30.69</td>
<td>Butane/Cyclopentane (50/50) 30.67</td>
</tr>
<tr>
<td>$P_{\text{el}}$ (kW)</td>
<td>192.39</td>
<td>205.73</td>
<td>219.78</td>
</tr>
<tr>
<td>$U_{\text{Heat}}$ (kWth/K)</td>
<td>23.47</td>
<td>25.31</td>
<td>26.39</td>
</tr>
<tr>
<td>$U_{\text{Cond}}$ (kWth/K)</td>
<td>56.33</td>
<td>61.44</td>
<td>68.28</td>
</tr>
<tr>
<td>$\dot{V}_{\text{exp, out}}$ (m$^3$/h)</td>
<td>2571.28</td>
<td>2442.09</td>
<td>1947.29</td>
</tr>
<tr>
<td>$n$ (RPM)</td>
<td>7357</td>
<td>8475</td>
<td>9258</td>
</tr>
<tr>
<td>SP (m)</td>
<td>0.045</td>
<td>0.042</td>
<td>0.038</td>
</tr>
<tr>
<td>VFR</td>
<td>44.43</td>
<td>48.37</td>
<td>54.53</td>
</tr>
</tbody>
</table>
4. Conclusions

A set of natural refrigerants and their binary mixtures were thermodynamically evaluated as working mediums for a WHR-ORC for three different heat source temperatures (150, 225 and 300°C), under subcritical and supercritical operating conditions. It was determined that especially for the lowest heat source temperature, the critical temperature of the working fluids (either pure or binary mixtures) has a major influence on the heat source utilization and the overall system exergetic efficiency. Moreover, it also affects the dependence of the latter on the maximum operation pressure of the cycle. In general, the performance of high critical temperature working fluids increases for high heat source temperatures (225 and mainly 300 °C). On the contrary, working fluids with low critical temperatures are preferable when the temperature of the heat source stream is lower (150 °C), since their exergetic efficiency is better (although usually at significantly higher operation pressures).

In almost all cases, the supercritical ORC can lead to the improvement of the system efficiency and smaller turbine size parameter values, at the expense of higher volume flow rates at the expander outlet, higher pressure and volume flow ratios in the turbine and increased rotational speeds.

The use of binary mixtures can further improve the cycle performance for all the cases that were examined, although it is often accompanied by increased UA values in the condenser. The exergetic efficiency of the zeotropic fluids is influenced by their component ratio. More specifically, the critical temperature (especially for lower heat source temperatures) of the working fluid and the temperature glide during its condensation are key parameters in determining the optimal composition. As a general rule, the second law efficiency tends to be maximized when the temperature glide closely matches the temperature increase of the cooling stream in the condenser and when the concentration of the most efficient pure component is higher. It should be also noted that the mixtures consisting of the most efficient pure components also tend to have the highest efficiency.

The supercritical ORC combined with the use of binary mixtures can result in substantial improvement of the exergetic efficiency. According to the cases investigated, the WHR-ORC exhibits the highest exergetic efficiency when the working fluid is a binary mixture and the maximum operation pressure is in the supercritical pressure range.

For heat source temperatures of 150 and 225 °C the natural refrigerants and their binary mixtures can be considered as appealing alternatives to R245fa since they do not only have a better thermodynamic performance, but they also generally exhibit favourable size parameter, volume flow ratio and turbine volume flow rate values, although they are associated with increased turbine rotational speeds. When the heat source is at 300 °C, despite their superior exergetic efficiency, their technical evaluation parameters are substantially inferior compared to R245fa. Consequently, further techno-economic investigations are required to determine if the benefits in the second law efficiency outweigh the apparent economic drawbacks that are associated with the use of these fluids.

References


