Techno-economic performance of the 2-propanol/1-butanol zeotropic mixture and 2-propanol/water azeotropic mixture as a working fluid in Organic Rankine Cycles

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Abstract

The techno-economic performance of the 2-propanol/1-butanol zeotropic mixture and 2-propanol/water azeotropic mixture as a working fluid in Organic Rankine Cycles (ORC) for waste heat recovery applications is analyzed. The ORC with two different architectures is modeled in the Aspen Plus V.10 environment for heat recovery from hot gases at 250 and 350°C with atmospheric and sub-atmospheric condensation scenarios. The results for three common working fluids in commercial ORCs are included to provide a practical comparison. The propanol/butanol mixtures (P/B) rich in propanol and propanol/water mixtures (P/W) with composition near the azeotropic point can result in 15 to 75% higher overall efficiencies compared to toluene and MM. Cyclopentane performs better than these mixtures when atmospheric condensation is considered. According to the economic assessment, the 55%P/45%W and 75%P/25%B mixtures lead to superior results for the atmospheric condensation scenario compared to other fluids. Also, it was found that only under a tailored boundary condition, the zeotropic mixture can perform superiorly compared to the most efficient component in the mixture.

Nomenclature

Symbols		Abbreviations	
C_p	specific heat capacity [kJ/kg.K]	APEA	Aspen process economic analyzer
h	specific enthalpy [kJ/kg]	AVA	available
$\dot{m}$	mass flow rate [kg/s]	CEPCI	chemical engineering plant cost index

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M	molar mass [kg/kmol]	COND	condenser
P	pressure [bar]	CR	critical
$\dot{Q}$	heat power [kW]	EOS	equation of state
T_b	boiling temperature [°C]	EVA	evaporator
T_{in}	heat inlet temperature [°C]	GWP	global warming potential
$T_{\circ}$	minimum allowable temperature [°C]	HC	heat carrier
$\dot{W}$	mechanical power [kW]	IHE	internal heat exchanger
Δp	Pressure drop [Pa]	KC	Kalina cycle
$\eta_{\circ}$	organic efficiency	MITA	minimum temperature approach
$\eta_{is,p}$	pump isentropic efficiency	ORC	organic Rankine cycle
$\eta_{is,t}$	turbine isentropic efficiency	REC	recuperator
η_{fan}	fan electric efficiency	SIC	specific investment cost
ρ_{air}	air density [kg/m^3]	VLE	vapor-liquid equilibrium
ϵ_{HR}	heat recovery factor	VLLE	vapor-liquid-liquid equilibrium
		P/B	2-propanol+1-butanol mixture
		P/W	2-propanol+water mixture

1. Introduction

In the last century, the increase in the usage of fossil energy sources has led to depleting these sources, global warming, and air pollution. In the last decades, the usage of renewable energy sources and waste heat recovery has been suggested to decrease the dependency on fossil fuels, lowering the emission of toxic gasses and greenhouse gasses, specifically CO_2. The heat available from renewable sources or waste usually is in lower temperatures. The conventional steam Rankine cycle does not allow efficient heat recovery below 370°C [1]. Considering water, the low molecular complexity and molar mass, high critical temperature, low condensation pressure, wet expansion in the turbine, high specific volume, and large specific enthalpy drop lead to expensive multistage turbines with high complexity in plant scheme. The use of organic fluids with low boiling temperatures in the Rankine cycle can help to exploit energy more efficiently from these low-temperature heat sources.

In the last two decades, many studies were published on Organic Rankine Cycles (ORCs). Several publications were based on fluid selections [2-6]. The working fluid should meet some requirements to be considered as a candidate in ORCs. Primarily, it should show acceptable thermodynamic and heat transfer properties, such as appropriate evaporation and condensation behavior, low specific volume, low liquid viscosity, and high liquid thermal conductivity. Also, environmental and safety concerns should be respected. GWP (global warming potential), ODP (ozone depletion potential), toxicity, and corrosiveness are the main environmental measures that should meet the regulations. Montreal

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Protocol [7] has banned some conventional working fluids which do not meet the requirements. Besides, an appropriate working fluid should be non-flammable and show favorable thermal resistance. However, in literature, a single fluid cannot be found that fulfills all the above-mentioned features.

Alcohols are usually considered as working fluids with unfavorable thermodynamic properties besides their flammability issues. However, their relatively lower costs, availability, and their low ODP and GWP can be some of the reasons for further studies on them as a working fluid in ORC systems. Alcohols with up to three carbon atoms are completely miscible in water [8]. On one side, the addition of water to alcohol can result in lower flammability hazards and improved thermodynamic properties for alcohol. Also, water represses the thermal decomposition of alcohols [9]. On the other side, the alcohol content in the mixture can lead to modifying the drawbacks of pure water in the Rankine cycle when the heat is available at lower temperatures [10]. Besides, alcohol/alcohol combinations can form zeotropic mixtures which show non-isothermal evaporation and condensation. The zeotropic mixtures are claimed to be beneficial as working fluid in ORC systems [11-14].

In literature, only a few publications studied alcohols and their mixtures. Tchanche et al. [15] did not suggest the use of alcohols for low-temperature ORC applications. Methanol and ethanol are more investigated among alcohols. Some authors proposed ethanol as a promising working fluid in engine waste heat recovery [16, 17]. Victor et al. [18] studied some pure alcohols and their mixtures with water as working fluid in an ORC and Kalina cycle. It was found that the water/methanol mixture was the most efficient working fluid among the fluids under their study for turbine inlet temperature between 220-250°C. Eller et al. [8] showed that the use of alcohol/alcohol mixture can increase the second law efficiency of the Kalina cycles instead of an ammonia/water mixture, especially when the heat source temperature is above 250°C. The same authors in [19] reported that KC with ethanol/hexanol delivers higher net power than KC with ammonia/water. Recently, Invernizzi et al. [10] studied water/organic compound mixtures with the intention of overcoming the limitations of pure water in RC for small power size and low-temperature heat sources in an ORC. Among the investigated mixtures, the water/2,2,2-trifluoroethanol mixture appeared as the most promising one.

ORCs employing multi-component, non-azeotropic working fluids featuring non-isothermal heat addition and heat rejection were analyzed by Angelino and Di Paliano [11]. The improved performance obtained with the two-component cycle is a direct consequence of the raised mean-heat addition temperature. Mixed fluids can reduce the internal entropy properly, but smaller temperature differences may lead to higher waste heat flow outlet temperature which will result in larger external entropy generation [20]. Chys et al. [12] reported that the use of a suitable zeotropic mixture has

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a positive effect on the ORC performance. The cycle efficiency increased by 15.7%, and an increase of 12.3% was obtained in generated electricity for heat source at 150°C. However, these increases were less pronounced for the higher temperature heat source. Also, they added that, in general, maximum temperature gradients are not equivalent to an optimal match with the temperature profiles and hence maximum efficiency. Kolahi et al. [21] reported that the maximum efficiencies usually occur in the mass fractions of 0.5 or 0.6 where temperature glides are also maximized. Lecompte et al. [13] found that using mixtures improves second law efficiency between 7.1% and 14.2% compared to pure working fluids. This improvement is due to the combination of higher heat input and higher heat conversion efficiency and is mainly related to decreased irreversibilities in the condenser. Whereas, Aghahosseini and Dincer [22] did not report any advantage of using zeotropic mixtures over pure fluids. Oyewunmi et al. [23] studied ORCs using large-glide alkanes and fluorocarbon mixtures as working fluid. They reported that, in the presence of a large amount of cooling fluid, cycles with the more volatile pure working fluids deliver greater power. These pure fluids are more efficient and cost-effective than those featuring working fluid mixtures. While mixtures as the working fluid are more efficient and produce higher power for limited or constrained cooling resources.

Based on the thermo-economic analysis, Heberle and Brüggemann [14] found that for temperatures about 160°C the additional heat exchange area for zeotropic mixtures of propane/isobutane, isobutane/isopentane, or R227ea/R245fa could be overcompensated by their higher performance regarding the most efficient pure fluids and lead to a lower electricity generation cost. The significant reduction of heat transfer coefficient at phase change for mixtures compared to pure fluids resulted in larger heat exchangers and consequently, higher specific investment cost (SIC) for mixtures. Propane/isobutane (20/80) had a SIC equal to 4,882 €/kW_e for heat source at 120°C.

In this paper, the azeotropic mixture of 2-propanol/water (P/W) and the zeotropic mixture of 2-propanol/1-butanol (P/B) are chosen to study the validity of the previously mentioned improvements in ORC systems for waste heat recovery. The P/W mixture was analyzed in Ref. [18] for a limited heat source temperature range. To the knowledge of the authors, the P/B mixture for the first time is analyzed in this work. Also, an economic assessment for thermodynamically optimized cycles is included to provide a practical comparison with common working fluids in commercial ORC systems.

2. Working fluids

Alcohol/alcohol binary mixtures are miscible, while only alcohols with up to three carbon atoms are fully miscible in water [8]. Considering the fully soluble alcohols in water, 2-propanol shows a semi-isentropic behavior compared to methanol and ethanol. Also,

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2-propanol is not among the fluids with high GWP and ODP and has a relatively lower price than famous organic fluids such as toluene and siloxanes family. Azeotropic mixture of 2-propanol/water shows favorable properties for ORCs application over the pure components. The addition of water to alcohol can result in higher performance, lowering the flammability hazard [10], repressing thermal decomposition [9], and overall lower price for the fluid. Also, the limitations of the pure water in the Rankine cycle with low-quality heat sources can be compensated.

Zeotropic mixtures can be considered as a working fluid to reduce irreversibilities associated with non-isothermal heat addition in ORC systems [24]. While some authors reported that higher heat conversion efficiency is mainly related to decreased irreversibilities in the condenser [13, 25]. Therefore, in general, a suitable mixture can provide a better match in the temperature profiles of heat exchangers. 1-butanol shows a semi-dry nature and can form a zeotropic mixture with 2-propanol. This mixture shows a maximum boiling point difference of 45°C between the components, so significant mixture fractionating does not occur [12].

In order to conduct a comparison, some of the main working fluids in commercial ORCs [26], such as MM from siloxanes, toluene from aromatics, and cyclopentane from hydrocarbons are included in this study. Besides, the efficiency behavior of an RC working with water is presented to indicate the effectiveness of using an alcohol-water mixture.

The VLE behavior of mixtures can be used to select the appropriate thermodynamic model, which can predict the thermodynamic properties of mixtures as working fluid in ORC systems. In Fig. 1, vapor-liquid equilibrium data for 2-propanol/1-butanol at 1.01 bar from Wang et al. [27] is plotted. They correlated their data using Wilson, NRTL, and UNIQUAC. It can be seen all these three models generating similar results.

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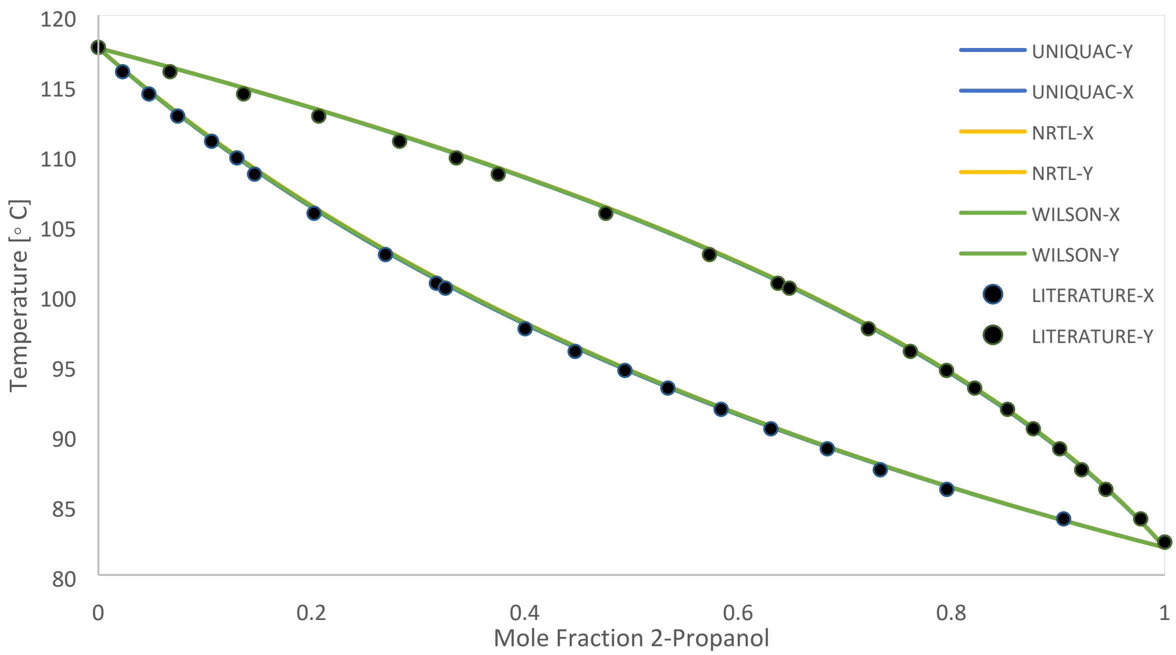

Fig. 1. T-x-y diagram for 2-propanol/1-butanol at 1.01 bar, ● Wang et al. [27] and numerical models.

The result of VLE for 2-propanol/water mixtures from Wilson and Simons [28] at 1.01 bar is shown in Fig. 2. As can be seen, UNIQUAC, NRTL, and WILSON are consistent with experimental results near azeotrope point and with compositions reach in 2-propanol. However, when the molar fraction of 2-propanol decreases NRTL is more consistent with the experimental results. Therefore, according to the published data from the literature, UNIQUAC and NRTL are chosen to predict the thermodynamic behavior of P/B and P/W mixtures, respectively. Thermodynamic properties of commercial fluids are described using the Peng-Robinson equation of state. The thermodynamic characteristics of the fluids under this study are listed in Table. 1. A combination of 75%/25%, 50%/50%, and 25%/75% are considered for mixture compositions on a molar basis. Later in the case of the P/W mixture, more compositions near the azeotrope point are analyzed.

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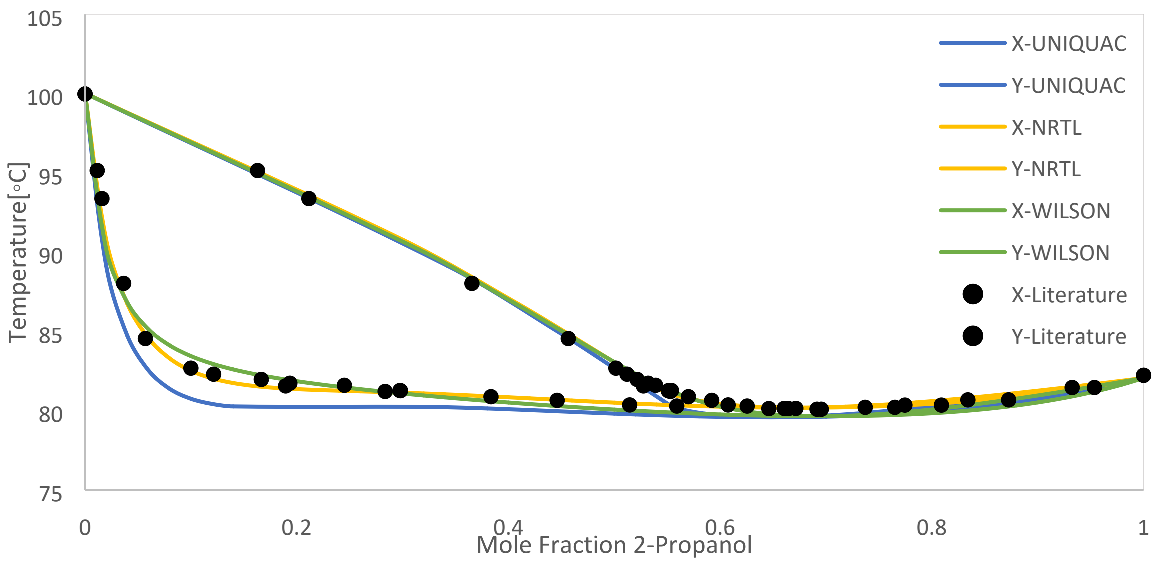

Fig. 2. T-x-y diagram for 2-propanol/water at 1.01 bar, ● Wilson and Simons [28] and numerical models.

Table. 1. Thermodynamic characteristics of fluids.

Working Fluid	M [kg/kmol]	ρ [kg/m^3]	T_b [°C]	P_{CR} [bar]	T_{CR} [°C]
2-propanol	60.1	785	82.5	47.7	235
1-butanol	74.12	810	117.7	43.4	289
75%P/25%B	--	793.1	96.5	38.45	242
50%P/25%B	--	799.1	105.5	38.28	257
25%P/75%B	--	803.5	112	39.14	271
75%P/25%W	--	805.9	79.5	47.9	236
50%P/50%W	--	834.4	82.5	58	252
25%P/75%W	--	881.2	92	75.8	279
Water	18.01	997	100	218.13	373
Toluene	92.14	867	110.6	41.09	318.65
MM	162.378	759.5	100.52	19.39	245.6
Cyclopentane	70.1	751	49	45.1	238.55

3. Cycle

The Rankine cycle is well known and widely studied in the literature. Plants based on the steam Rankine cycle are complicated and consist of many components. Different architectures of ORCs are studied [24]. In this work, basic ORC and recuperated ORC working in subcritical conditions are assumed. A schematic of basic ORC and recuperated ORC are shown in Fig. 3 and 5, respectively.

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A basic ORC includes four components. The compressed working fluid leaves the pump and enters a heat exchanger to be evaporated (stream 2). A heat carrier supplies energy to the cycle (stream 5). The high pressure and temperature saturated vapor (stream 3) expands in the turbine, which delivers mechanical power. Low-pressure flow (stream 4) condenses in a heat exchanger which is cooled by air (stream 7). Then the pressure of the saturated liquid (stream 1) is increased by the pump, and the cycle continues. Fig. 4 shows the T-s diagram of a basic ORC for 75%P/25%B mixture. The cycle operates with an evaporation pressure equal to 18 bar, and condensation occurs at 0.1 bar. The temperature glide during evaporation and condensation is evident.

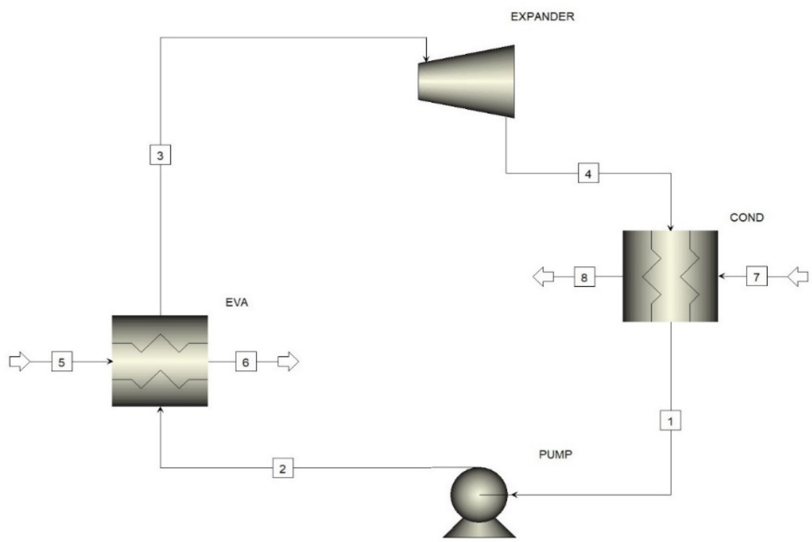

Fig.3. Schematic of basic ORC.

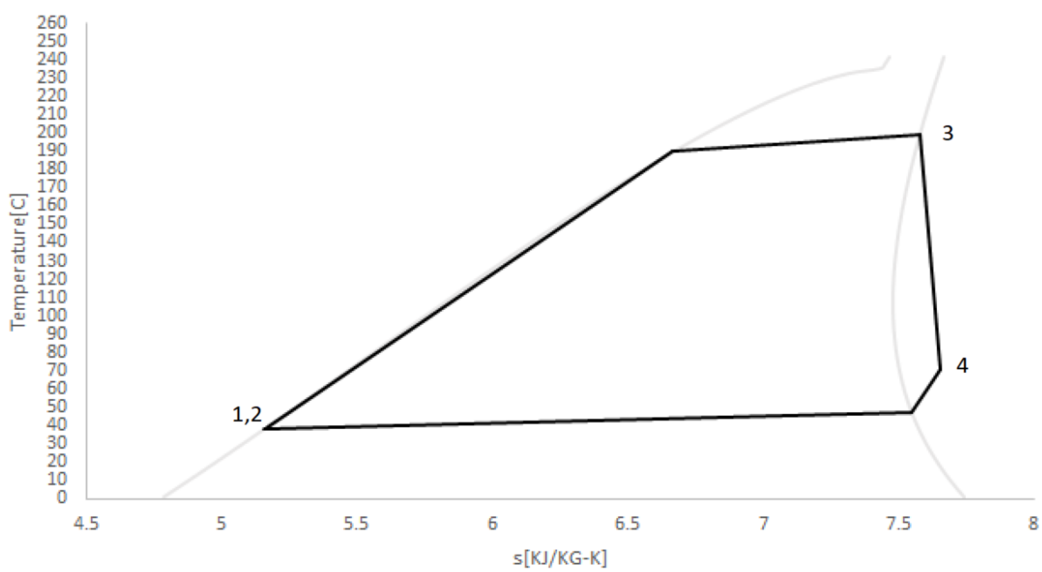

Fig. 4. T-s diagram of a basic ORC for 75%P/25%B.

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Recuperated ORC is designed to extract the available heat from the superheated fluid after expansion. Expanded superheat flow (stream 4) enters an internal heat exchanger (IHE) and cooled down to enter the condenser (stream 4A). High-pressure flow (stream 2) is preheated before entering the evaporator (stream 2A). The remaining processes are similar to basic ORC. The T-s diagram of a recuperated ORC working with cyclopentane is presented in Fig. 6.

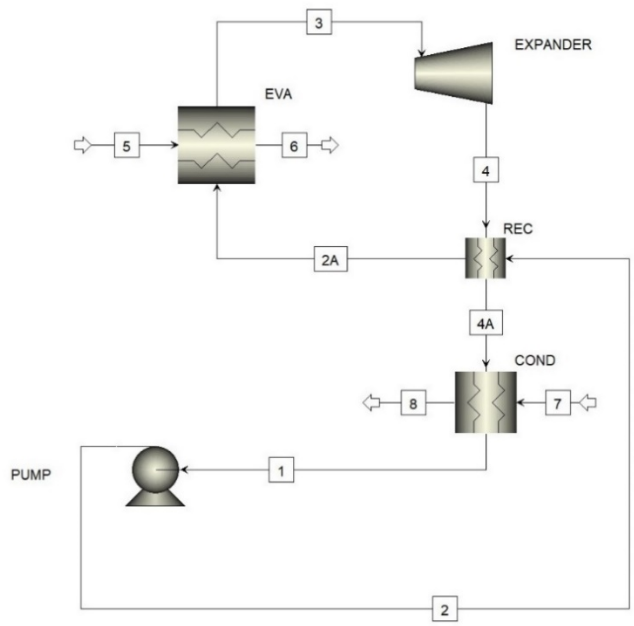

Fig. 5. Schematic of ORC with Recuperator (+IHE).

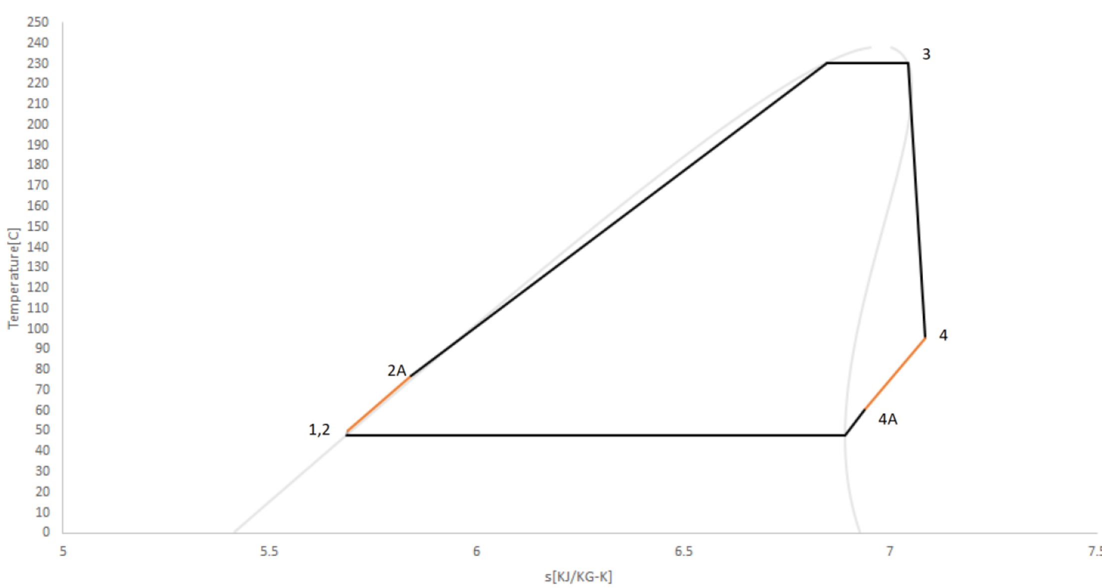

Fig. 6. T-s diagram of an ORC with Recuperator (+IHE) for cyclopentane.

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In the following, the governing equations and performance indicators are presented. Firstly, the heat input for basic ORC and recuperated ORC is calculated using equations (1) and (2), respectively:

$$\dot{Q}_{EVA} = \dot{m}(h_3 - h_2) \tag{1}$$

$$\dot{Q}_{EVA,REC} = \dot{m}(h_3 - h_{2A}) \tag{2}$$

The turbine is considered isentropic and the work is described as:

$$\dot{W}_{Turbine} = \dot{m}(h_3 - h_{4,is}) \times \eta_{\ is,t} \times \eta_{\circ} \tag{3}$$

The pump work is defined in Eq. (4):

$$\dot{W}_{Pump} = \dot{m}(\frac{h_{2,is} - h_1}{\eta_{is,p} \times \eta_{\circ}}) \tag{4}$$

The work of the condenser fan is calculated as follows:

$$\dot{W}_{Fan} = \frac{\dot{m}_{air} \ \times \Delta p_{Fan}}{\rho_{air} \times \eta_{Fan}} \tag{5}$$

A design pressure drop of 170 Pa [29], and a fan electrical efficiency equal to 75% are assumed.

The net power output of the cycle is defined in Eq. (6):

$$\dot{W}_{Net} = \dot{W}_{Turbine} - (\dot{W}_{Pump} + \dot{W}_{Fan}) \tag{6}$$

Cycle efficiency is calculated using Eq. (7):

$$\eta_{Cycle} = \frac{\dot{W}_{Net}}{\dot{Q}_{EV}} \tag{7}$$

A major part of the publications on ORCs is dedicated to cycle efficiency or second law efficiency. In this study, besides the cycle efficiencies, the performance of the cycles is compared based on overall efficiency. $\eta_{Overall}$ is a suitable indicator for waste heat recovery applications [30] and is defined in Eq. (8):

$$\eta_{Overall} = \eta_{Cycle} \times \epsilon_{HR} \tag{8}$$

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The heat recovery coefficient (ϵ_{HR}) measures the ability of the cycle to absorb heat from the energy source and is defined as the ratio of heat input to cycle and available heat from heat carrier (Q_{AVL}). The available heat is calculated from Eq. (9):

$$\dot{Q}_{AVL} = \dot{m}_{HC} \times C_{p,HC} \times (T_{in} - T_{\circ}) \tag{9}$$

where $\dot{m}_{HC}$ and $C_{p,HC}$ are the mass flow rate and specific heat of the heat carrier, respectively. $T_{\circ}$ is the minimum allowable temperature for heat carrier at the exit of the evaporator.

4. Simulation and assumptions

4.1. Thermodynamics

Basic ORC and recuperated ORC are modeled in the Aspen Plus V.10 environment [31]. A flow of hot air with two different temperatures (250, or 350°C) is assumed as a heat carrier. Also, for further analysis of the influence of the heat source temperature on the cycle performance, the same heat carrier is assumed with temperatures from 200 to 500°C. On the one hand, organic fluids are all useless above 350-400°C [32]. On the other hand, in waste heat recovery applications, usually, temperatures are below 350°C [24]. So, temperatures higher than thermal stability limits are only considered for studying the efficiency trends. For the sake of generality, hot air is assumed as the heat carrier. For industrial waste heat recovery applications, hot air or flue gases are the primary heat carriers. For example, in the cement industry, hot air from the clinker cooler has a temperature of around 280-360°C [33]. The minimum temperature that the heat carrier can be cooled is set at 60°C to investigate the capability of working fluids for heat recovery from lower temperatures. However, in the case of flue gases, the typical value of this temperature limit is around 100-130°C to avoid condensation of acidic gases [24]. Considering the flue gases from natural gas combustion, the minimum allowable temperature for the flue gases at the exit of the evaporator can be around 70°C [34]. A summary of design conditions is reported in Table 2.

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Table. 2. Design conditions.

Property	Value	Unit
Main heat source temperature, T_5	250-350	˚C
Heat carrier mass flow rate	10	Kg/s
Available heat	1930-2967	kW
Heat source temperature for sensitivity analysis	200-300-400-500	˚C
Available heat for sensitivity	1.4-2.5-3.5-4.5	MW
Cooling air temperature, T_7	15	˚C
Pressure drop in the condenser	2%	--
Minimum temperature approach in the evaporator	7.5	˚C
Minimum temperature approach in the condenser	5	˚C
Minimum temperature approach in IHE	10	˚C
Turbine isentropic efficiency	0.9	--
Pump isentropic efficiency	0.8	--
Turbine and pump organic efficiency	0.98	--

A maximum pressure level equal to 50 bar is imposed to enable the possibility of studying the performance of the working fluids over a wider range of pressures. In practice, maximum pressure is limited to 30 bar [35] due to safety procedures and higher plant costs for higher operating pressures. The evaporation pressures are chosen in a way that maximizes overall efficiency. Two constraints are applied to pressures. Firstly, if optimum evaporation pressure is around critical pressure, the pressure is limited to $0.9P_{CR}$. Secondly, if the optimum pressure is over 50 bar, evaporation pressure is limited to 50 bar.

Cooling air entering the condenser is assumed at 15°C. This temperature enables condensation at even lower pressures. In contrast to most of the publications, two general condensation scenarios are considered with predefined pressures in this work: An atmospheric and a sub-atmospheric condensation pressure. The literature states that the lower limit of condensation pressure due to technical limits is 0.05 bar (5 kPa) [36, 37]. So, the sub-atmospheric condensation pressure is set at 0.1 bar for all the fluids under this study except for cyclopentane which condenses at 0.4 bar due to the lower condensation temperature compared to the other fluids. Based on the results of Ref. [23], a case study is performed in Section 5 to investigate the effect of the external heat source/sink conditions on the overall efficiency of ORCs using zeotropic (P/B) mixture.

Superheating is only considered for P/W mixtures due to the tendency of wet expansion in the turbine. The superheating is limited to 6 and 8°C for atmospheric and sub-atmospheric condensations, respectively. Few degrees of superheating are preferred for ORCs [20]. The minimum temperature approach (MITA) in heat exchangers in real ORC

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plants is at least 5°C [38]. In this work, MITA in the evaporator is set at 7.5°C and, if it is necessary, increased by a 2.5°C step to keep the exit heat carrier temperature over 60°C. Also, MITA in IHE is set at 10°C to avoid any condensation during the recuperation.

The isentropic efficiency of the axial turbine is assumed to be constant and equal to 90% in this work. Turboden [39] claims for manufacturing ORC turbines with this isentropic efficiency. However, in practice, turbine isentropic efficiency can be varied based on the working condition and the working fluid. According to the results in Ref. [40], the turbine isentropic efficiency can be kept close to 90% using multistage axial turbines.

Firstly, the results generated by the models of this study are compared with the literature for commercial fluids. The boundary conditions for this part are assumed according to the related literature. The difference in the results is around 1%. This small deviation in results is due to the different equations of state that are used in the literature and this study. The EOS used in the literature is specifically calibrated for the fluids, while in this study, Peng-Robinson EOS is used for the commercial fluids. The detailed data for cycle validation is reported in Table 3.

Table. 3. Result of ORC validation.

Working Fluid	P_{EVA} [bar]	$T_{Turbine\ Inlet}$ [˚C]	Cycle Type	$T_{Heat\ Carrier}$ [˚C]	EOS Used in Literature	η_{Cycle} % This Work	η_{Cycle} % Literature	Error %
Toluene (+IHE)	32.2	301.5	Subcritical	350	BACKONE	20.59	20.7[5]	0.55
MM (+IHE)	17.451	239.4	Subcritical	380	Span-Wagner	21.85	22.2[37]	1.60
Cyclopentane (+IHE)	40.6	300	Superheat	350	BACKONE	23.28	23.6[5]	1.37

4.2. Economic analysis

The mixtures under this study with compositions that show the highest overall efficiency are selected for an economic assessment to compare with the commercial fluids. Aspen Process Economic Analyzer (APEA) [31] is used to estimate the installed cost for each piece of equipment. APEA uses different input data such as pressure, temperature, and flow rate of each equipment to preliminary size it and, consequently, determining the capital cost from its database [41]. The costing module evaluates economics based on Icarus technology. The approach used in the technology does not rely on capacity-factored curves for equipment sizing, nor does it rely on factors to estimate installation quantities and installed cost from bare equipment cost. Instead, it follows industry-standard design codes and procedures to represent equipment with associated plant bulks and cost modeling and scheduling methods to estimate the cost of the project [42].

Aspen is not able to calculate the cost of the turbo-expander for sub-atmospheric condensation. Similar results are obtained from Turton [43] for atmospheric

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condensation. So, the cost of the axial turbine is calculated based on Turton for the sub-atmospheric condensation scenario. Turton's approach estimates costs based on the prices of 2001 in USD. These costs are updated to 2020 using CEPCI and then converted to euros. The total investment cost is considered to be the sum of the installed component costs. Specific investment cost (SIC) expressed in €/kW is applied to enable a fair comparison considering the power output of each ORC with different working fluids.

$$SIC = \frac{Total\ Installed\ Cost}{\dot{W}_{NET}} \tag{10}$$

5. Results and discussion

5.1. Mixture composition

The performance of different mixture compositions is compared based on the overall efficiency. Fig. 7a and b present the overall efficiency of ORCs using P/B mixtures as a function of 2-propanol mole fraction under two different heat source temperatures and two condensation scenarios. The pure propanol and 75%P/25%B always show higher overall efficiencies for both heat sources compared to other compositions. Overall efficiency decreases with the decrease of propanol content. This value varies from less than 6% for pure butanol under 250°C of the heat source and atmospheric condensation condition to more than 26% for pure propanol under the higher heat carrier temperature and sub-atmospheric condensation scenario. For condensation at 1 bar, in Fig. 7a, efficiency lines for both cycle types are overlapped, so the use of IHE does not bring an advantage for 350°C of the heat source. While a 4% increase in overall efficiencies can be obtained using a recuperator for lower heat source temperature only for the mixtures. As can be seen in Fig. 7b, recuperated cycles perform slightly better except for mixtures rich in butanol for higher heat source temperature. The increase in overall efficiency is still small, so performing an economic assessment becomes necessary to understand if the additional cost of the recuperator can be overcompensated by the excess power output. However, the use of a recuperator can be beneficial for a higher cooling limit of the heat carrier [5, 24]. As shown in Fig. 7a and b, zeotropic mixtures do not improve overall efficiency under the predefined boundary conditions in section 4.1. The effect of boundary conditions on zeotropic mixture performance will be discussed in detail in section 5.3.

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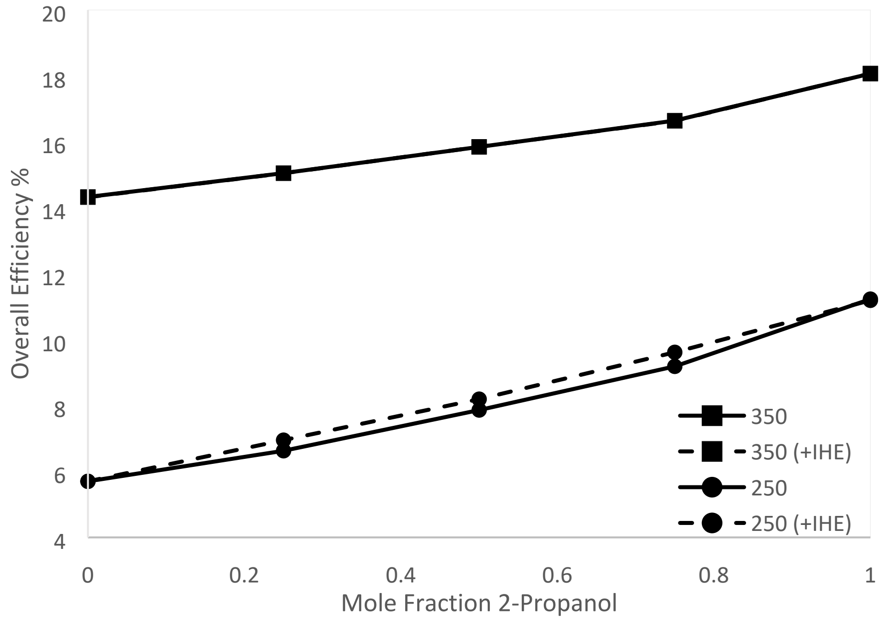

Fig. 7a. Overall efficiency as a function of 2-propanol mole fraction in 2-propanol/1-butanol zeotropic mixture for 2 different heat source temperatures. Solid lines for basic cycle, dashed lines for cycle with recuperator. (a) atmospheric condensation, (b) sub-atmospheric condensation.

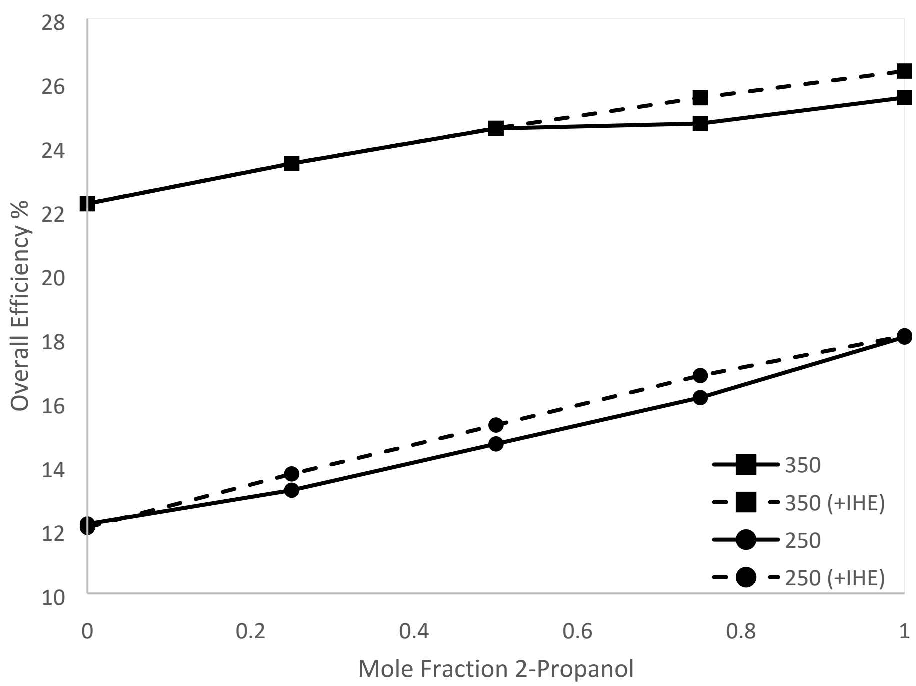

Fig. 7b. Overall efficiency as a function of 2-propanol mole fraction in 2-propanol/1-butanol zeotropic mixture for 2 different heat source temperatures. Solid lines for basic cycle, dashed lines for cycle with recuperator. (a) atmospheric condensation, (b) sub-atmospheric condensation.

Similar to P/B mixtures, overall efficiencies for P/W mixtures over mole fraction of 2-propanol are plotted in Fig. 8a and b for condensation at 1 and 0.1 bar, respectively. Pure

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propanol has a superior performance under 250°C of the heat source in both condensation scenarios. While for the heat source at 350°C, considering both condensation pressures, mixtures with composition near the azeotrope point show superior performance compared to pure propanol. A propanol content equal to 65-70% on a molar basis is assumed near the azeotrope point. ORC using 65%P/35%W can result in an almost 5% increase in overall efficiency compared to pure propanol for higher heat source temperature and atmospheric condensation. Therefore, water addition to propanol enables better performance for higher heat source temperatures. However, it should be noted that the wet expansion at the turbine for mixtures with higher water content is unfavorable for turbine performance and structure. The presence of liquid at the outlet of turbines becomes more severe for sub-atmospheric condensation. Also, lower heat source temperatures may lead to wet expansion. Since lower evaporation pressures should be used, which results in wet expansion due to the shape of the T-s diagram.

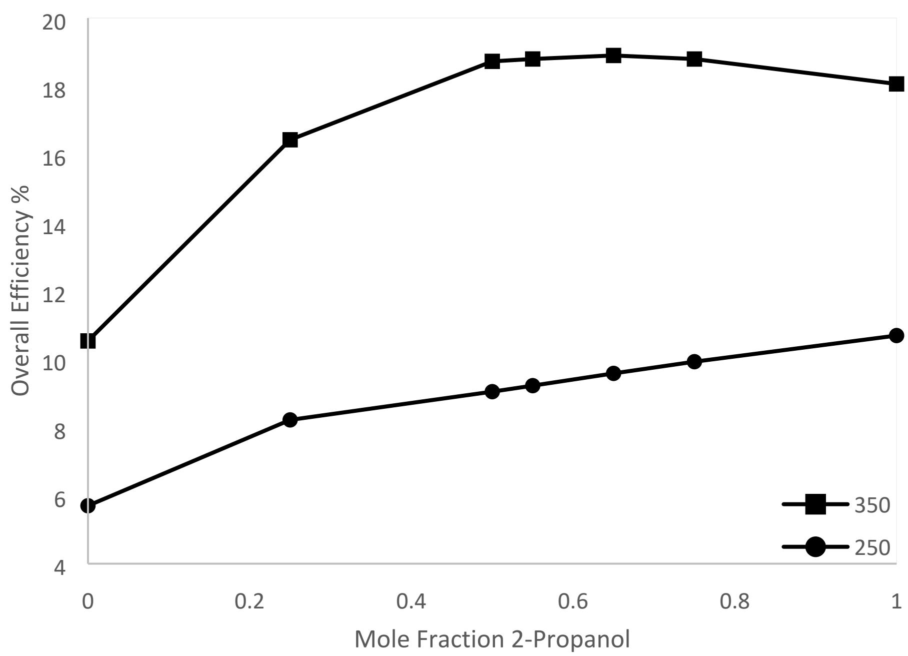

Fig. 8a. Overall efficiency as a function of 2-propanol mole fraction in 2-propanol/water azeotropic mixture for 2 different heat source temperatures. (a) atmospheric condensation, (b) sub-atmospheric condensation.

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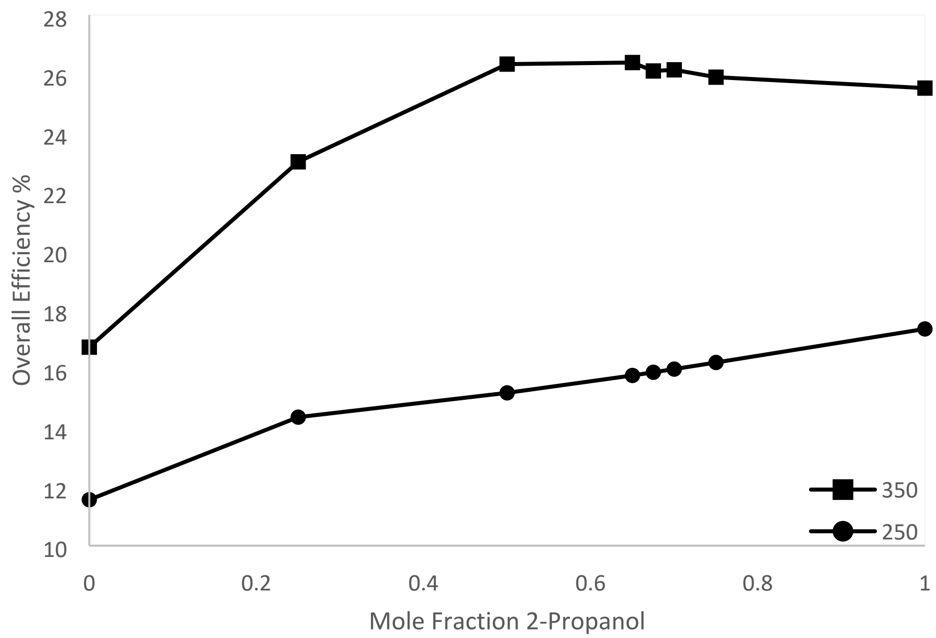

Fig. 8b. Overall efficiency as a function of 2-propanol mole fraction in 2-propanol/water azeotropic mixture for 2 different heat source temperatures. (a) atmospheric condensation, (b) sub-atmospheric condensation.

The simulation results of ORCs using pure and mixed fluids working under 350 and 250˚C of the heat sources are reported in Tables. 4 and 5, respectively. Working fluids are labeled with (+IHE) when the recuperated cycle performs more efficiently than basic ORC. Listed mixtures show higher overall efficiencies compared to other compositions. Also, for P/W mixtures, dry expansion is considered as a selection factor. Inevitably, under lower heat source temperature with sub-atmospheric condensation, the vapor quality at the turbine outlet is 0.98 for the mixture of 75%P/25%W.

Under the 350˚C of the heat source and atmospheric condensation scenario in Table. 4, the highest performance is obtained by a recuperated ORC using cyclopentane with an overall efficiency equal to 21.38%. Next, the mixture of 65%P/35%W delivers higher net power output compared to other working fluids. The cycle efficiency is 21.38%, and it is slightly lower than the cycle efficiency for pure propanol in a recuperated cycle (21.48%), but due to a better heat recovery for the mixture, higher overall efficiency can be obtained with 65%P/35%W. Finally, the mixture of 75%P/25%B delivers a 13.6% lower net power output compared to the selected P/W mixture.

For the sub-atmospheric condensation scenario, all three performance parameters increase with respect to the atmospheric condensation pressure. Only the cycle efficiency for cyclopentane slightly decreases due to higher fan power consumption. The higher heat recovery factor for the cycle with sub-atmospheric condensation overcompensates the reduction of cycle efficiency, so the overall efficiency does not sink for ORC (+IHE) with cyclopentane. The best performance is for propanol in a recuperated cycle with an overall

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efficiency equal to 26.36%. The mixture of 75%P/25%B (+IHE) shows higher cycle efficiency with respect to pure propanol, but a lower heat recovery level results in lower overall efficiency (25.52%). The 70%P/30%W mixture delivers higher net power output than the P/B mixture, leading to an overall efficiency equal to 26.14%. The overall efficiencies increase up to 75% for MM and toluene when condensation pressure sinks to 0.1 bar.

Considering the heat source at 250°C, a steep reduction in performance factors is evident in Table. 5. Lower cycle efficiencies due to lower optimum evaporation pressures and smaller heat recovery ability result in lower overall efficiencies. This reduction is more pronounced for working fluids with higher T_b and T_{CR}. Toluene and 1-butanol result in the lowest overall efficiencies when atmospheric condensation is considered (5.55 and 5.70%, respectively). This value can increase up to 150% for toluene in a recuperated ORC with sub-atmospheric condensation. Cyclopentane still performs superiorly for condensation at 1 bar, with an overall efficiency equal to 14.76%. As shown previously in this section, mixtures deliver lower net power output compared to pure propanol. For cycles with atmospheric condensation, the 75%P/25%W mixture results in around 3% higher overall efficiency compared to 75%P/25%B, while in the sub-atmospheric scenario, the P/B mixture delivers higher net power.

Table. 4. Simulation results for the ORC applied to 350°C of the heat source.

Working Fluid	P_{COND} [bar]	P_{EVA} [bar]	T_{EVA} [°C]	$\dot{m}$ [kg/s]	P_{Gross} [kW]	P_{Pump} [kW]	P_{Fan} [kW]	η_{Cycle} %	ϵ_{HR} %	$\eta_{Overall}$ %
2-propanol (+IHE)	1	42	227	2.79	562.9	-20.4	-6.3	21.48	84.14	18.07
1-butanol	1	40	283	2.39	444.8	-16.7	-3.0	19.09	75.07	14.33
Water	1	23	226	0.68	317.8	-2.0	-3.4	19.14	55.02	10.53
Toluene	1	20	265	3.70	383.0	-11.5	-3.0	17.21	72.18	12.42
MM (+IHE)	1	17.5	239	7.10	361.7	-22.0	-3.5	18.11	62.56	11.33
Cyclopentane (+IHE)	1	40.6	230	5.10	684.5	-35.8	-14.2	23.31	91.76	21.38
75%P/25%B	1	35	236	2.75	515.3	-16.5	-5.0	18.93	87.91	16.64
65%P/35%W	1	47	235	2.19	584.8	-17.2	-6.8	21.38	88.40	18.90
2-propanol (+IHE)	0.1	42	227	2.76	831.7	-19.0	-30.7	26.38	99.90	26.36
1-butanol (+IHE)	0.1	40	283	2.40	682.1	-15.9	-7.4	28.34	78.36	22.20
Water	0.1	12	196	0.80	510.2	-1.2	-12.5	23.83	70.21	16.73
Toluene (+IHE)	0.1	13	236	4.22	680.6	-8.2	-13.4	27.38	81.11	22.21
MM (+IHE)	0.1	17.5	239	6.56	630.6	-19.4	-18.1	27.36	73.08	19.99
Cyclopentane (+IHE)	0.4	40.6	230	5.11	850.9	-35.1	-137.9	22.89	99.83	22.85
75%P/25%B (+IHE)	0.1	35	236	2.75	788.3	-15.7	-15.4	26.44	96.54	25.52
70%P/30%W	0.1	46	236	2.22	826.8	-16.2	-35.0	26.33	99.29	26.14

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Table. 5. Simulation results for the ORC applied to 250°C of the heat source.

Working Fluid	P_{COND} [bar]	P_{EVA} [bar]	T_{EVA} [°C]	$\dot{m}$ [kg/s]	P_{Gross} [kW]	P_{Pump} [kW]	P_{Fan} [kW]	η_{Cycle} %	ϵ_{HR} %	$\eta_{Overall}$ %
2-propanol	1	23	193	1.41	225.4	-5.5	-3.2	17.42	64.48	11.23
1-butanol	1	7	186	1.35	113.2	-1.5	-1.7	11.35	50.23	5.70
Water	1	8	176	0.36	112.2	-0.3	-1.9	12.99	43.86	5.70
Toluene	1	6	190	1.88	110.1	-1.5	-1.5	11.94	46.48	5.55
MM	1	7	184	4.27	147.1	-4.8	-2.1	9.98	72.76	7.26
Cyclopentane (+IHE)	1	17	171	2.86	300.9	-8.1	-8.0	19.65	75.10	14.76
75%P/25%B (+IHE)	1	17	197	1.37	191.9	-3.9	-2.5	16.59	57.95	9.62
75%P/25%W	1	18	184	1.14	198.1	-3.4	-3.2	16.46	60.28	9.92
2-propanol (+IHE)	0.1	18	181	1.55	370.4	-4.6	-17.2	22.24	81.23	18.07
1-butanol	0.1	6	179	1.48	241.0	-1.4	-4.6	18.09	67.28	12.17
Water	0.1	4	152	0.47	231.0	-0.2	-7.7	18.54	62.35	11.56
Toluene (+IHE)	0.1	3	156	2.79	284.2	-1.2	-8.8	19.25	73.77	14.20
MM (+IHE)	0.1	6	176	4.54	332.7	-4.6	-12.5	22.55	72.53	16.36
Cyclopentane (+IHE)	0.4	14	160	3.10	398.3	-7.2	-83.6	18.24	87.32	15.93
75%P/25%B (+IHE)	0.1	10	172	1.66	336.6	-2.7	-9.3	20.35	82.65	16.82
75%P/25%W	0.1	11	165	1.35	335.0	-2.3	-19.7	20.34	79.72	16.21

5.2. Sensitivity analysis

The behavior of the overall efficiencies of the selected fluids is investigated by applying a sensitivity analysis on the heat source temperature from 200 to 500°C. Considering that the temperatures above 350-400°C are not practical for waste heat recovery applications using organic fluids [24, 32]. The recuperated ORC is chosen for propanol/butanol mixtures and commercial fluids due to slightly superior performance in higher temperatures. Also, pure propanol in basic ORC with 6 degrees of superheating is chosen to provide a comparison with propanol in recuperated ORC. The composition of propanol/water mixture is chosen near the azeotropic point which shows higher efficiency for medium temperature heat source and a dry expansion over a wider range of heat carrier temperatures. The trend of overall efficiencies as a function of heat carrier temperature is plotted in Fig. 9 and 10 for atmospheric and sub-atmospheric condensation pressures, respectively.

When condensation occurs at atmospheric pressure, cyclopentane shows the highest efficiency over the whole temperature range. The overall efficiency starts at 10.5% for 200°C and reaches 22% for 500°C of the heat source. The superior performance of cyclopentane for condensation at 1 bar can be explained by its lower boiling point compared to other fluids under this study. This low boiling point allows higher heat recovery. Also, cycle efficiencies are higher for ORC with cyclopentane as a medium compared to other fluids in the atmospheric condensation scenario. Propanol has the

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second-highest efficiency from 200 to 300°C. The P/B and P/W mixtures have lower efficiencies than propanol up to 300°C. By increasing the temperature, the P/W mixtures can reach higher efficiency levels. The second most efficient fluid for temperatures over 350°C is the 55%P/45%W mixture. The mixture of 75%P/25%B has the lowest performance among the selected mixtures for this comparison, with an overall efficiency equal to 5.3% at 200˚C, and 18% for heat source at 500˚C. As is evident in Fig. 9, butanol, MM and toluene are among the working fluids with the lowest performance. These fluids become more efficient for higher temperatures.

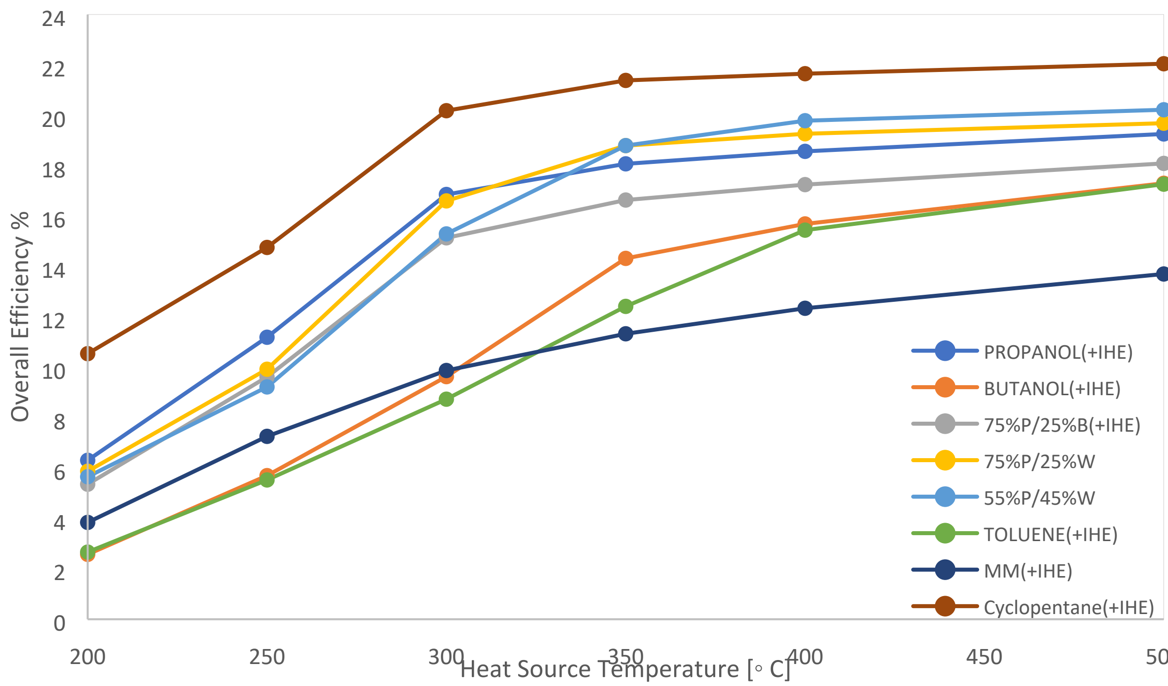

Fig. 9. General comparison among working fluids based on overall efficiencies for condensation at 1 bar.

For sub-atmospheric condensation, MM, superheated propanol, 70%P/30%W, 75%P/25%B, and cyclopentane show efficiencies from 12.6 to 11.4 % when heat source temperature is 200°C. Propanol in a recuperated ORC with 18.06% has the highest efficiency for heat carrier at 250°C. At 300°C, propanol still performs more efficiently, and the 70%P/30%W and 75%P/25%B mixtures are the next candidates. For heat source at 350°C, 70%P/30%W, and propanol in ORC with IHE show overall efficiencies over 26%. They are followed by 75%P/25%B with 25.5%. At 500°C, toluene becomes the most efficient fluid with an efficiency of over 27%. It should be recalled that the superior performance for sub-atmospheric condensation is obtained with the cost of the more complicated turbines, larger condensers, more advanced sealings, a pump for the evacuation of infiltrating air in the condenser, and in general, more expensive plants.

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The performance for all working fluids under this study increases with heat source temperature. For most of the fluids, the rate of increase is higher in the range of 200 to 350°C. With increasing the heat source temperature, the optimum evaporation pressure level increases, which enables higher cycle efficiencies. Also, the heat recovery factor increases with the increase of heat source temperature. Butanol, toluene, and MM in a recuperated cycle continue their increase in overall efficiency even after 350°C. This trend can be explained by considering higher critical temperatures for butanol and toluene, which postpones the higher optimum evaporation pressures to higher heat source temperatures. Butanol reaches its maximum evaporation pressure at 40 bar under the 350°C of the heat source. Increasing the heat source temperature leads to move the MITA to the preheating section of the evaporator. When the pinch point moves to the inlet of the preheating, more heat can be recovered from the heat source [14]. Toluene reaches its maximum evaporation pressure (39 bar) with temperatures higher than 350°C. With the heat source at 400°C, the pinch point is at the inlet of the preheater for toluene and butanol. However, due to the high temperatures of the saturated liquid after the recuperator, the maximum heat recovery cannot be obtained. This is also true for MM, so increasing the heat source temperature results in higher heat recovery and consequently higher overall efficiency. For the fluids with lower boiling points, such as cyclopentane, propanol, and mixtures with high propanol content, overall efficiency reaches an almost straight line after 350°C. Also, at higher temperatures, a small decrease occurs for these fluids. Since the maximum evaporation pressure is enabled at lower temperatures and heat recovery reaches its maximum, further increase in heat source temperature has a negative effect on overall efficiency. It means the heat content increases faster than the maximum recoverable heat by employing these fluids.

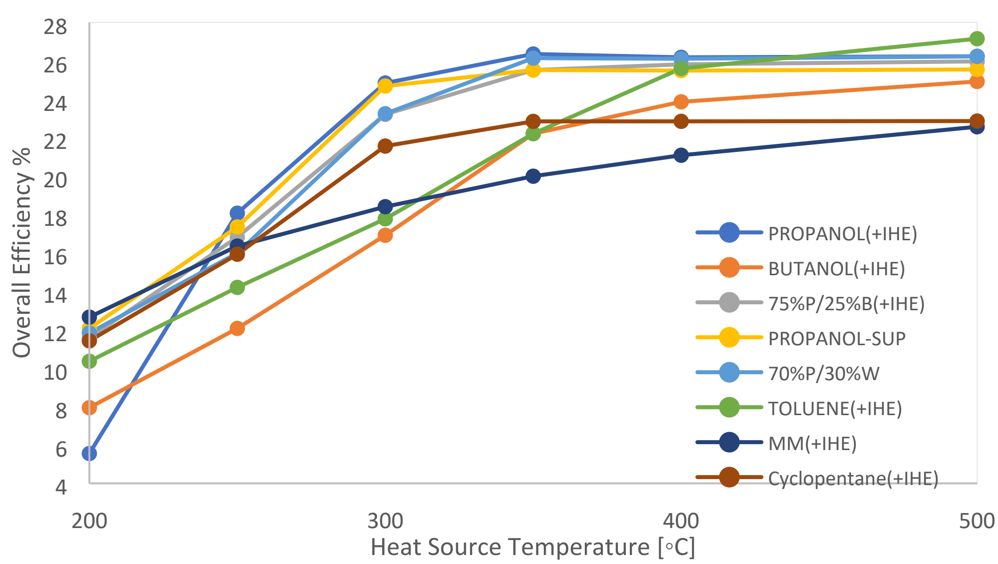

Fig. 10. General comparison among working fluids based on overall efficiencies for condensation at 0.1 bar (Cyclopentane condenses at 0.4 bar).

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5.3. Effect of boundary conditions on zeotropic mixture performance

As it was illustrated in Fig. 7.a and b, P/B zeotropic mixtures do not perform better than pure propanol, while some authors [11-14] reported that better performance can be obtained using zeotropic mixtures. Assumed boundary conditions in this study caused this deviation. Fix condensation pressure for pure and mixture fluids can be the main reason for this phenomenon. In order to investigate the effects of different boundary conditions, a case study considering a basic ORC is conducted. Heat carrier temperature is varied between 250 and 350°C to study the effect of heat source on the overall efficiency for different zeotropic mixture composition. In contrast to the fixed condensation pressures assumed in Section 4.1, here, the condensation pressure is varied to lower values considering an almost 10°C glide in cooling air temperature for two different ambient temperatures: a. 15°C, b. 30°C.

The overall efficiency as a function of mole fraction of 2-propanol in the zeotropic mixture under different heat source/sink conditions is plotted in Fig. 9. For 250°C of the heat source, similar to Section 5.1, pure propanol shows superior performance compared to the mixture. So, the result of this heat source is not reported here. It can be stated that 250°C is not a suitable heat source temperature for the P/B mixture. Since this temperature cannot activate higher optimum evaporation pressures when butanol with its higher boiling point is present in the mixture. Increasing the heat source temperature to higher levels changes the overall efficiency trend. Considering the 300°C of the heat source, the 75%P/25%B mixture can lead to almost 1% higher overall efficiency (net power output) than propanol as the most efficient pure fluid in this mixture under both heat sink conditions. It is interesting to note that pure propanol results in higher gross power compared to mixtures and that the superior performance of the 75%P/25%B mixture is only due to the lower air condenser fan power consumption. While for the 350°C of the heat source, the highest net power output is coincident with the highest gross power. Under the heat sink condition (a), pure butanol can deliver the highest power output. This higher performance for pure butanol is mainly caused by a higher cycle efficiency and a larger heat recovery factor which is obtained by a very low condensation pressure (0.011 bar). On the contrary, when the air cooler temperature is increased to 30°C in heat sink condition (b), higher condensation pressures should be applied. Therefore, the heat recovery factor for pure butanol decreases and results in higher overall efficiency for 25%P/75%B mixture. However, this increase in performance is only around 1%. In general, when the mixture performs more efficiently than pure fluid, the corresponding composition results in the best match in the temperature profiles of the condenser.

Based on the results obtained in section 5.1 and here, it can be said that the performance of zeotropic mixtures cannot be easily predicted. Considering a fixed condensation pressure, propanol always shows the highest overall efficiencies. Also, for variable condensation pressure, when the heat source temperature is 250°C or lower, propanol

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results in superior performance. Mixtures can show higher overall efficiencies compared to pure fluids if the heat source temperature increases to 350°C. Rising the heat carrier temperature leads to higher performance for mixtures rich in propanol, and the further increase can result in higher overall efficiencies for mixtures rich in butanol. Under a specific boundary condition, pure butanol becomes the most efficient fluid in the mixture. Therefore, the choice of the optimum working fluid (pure or mixture) is sensitive to the particular external heat source/sink conditions that the cycle is required to interface with thermally, and moreover, in a non-trivial fashion, that would be hard to expect intuitively [23].

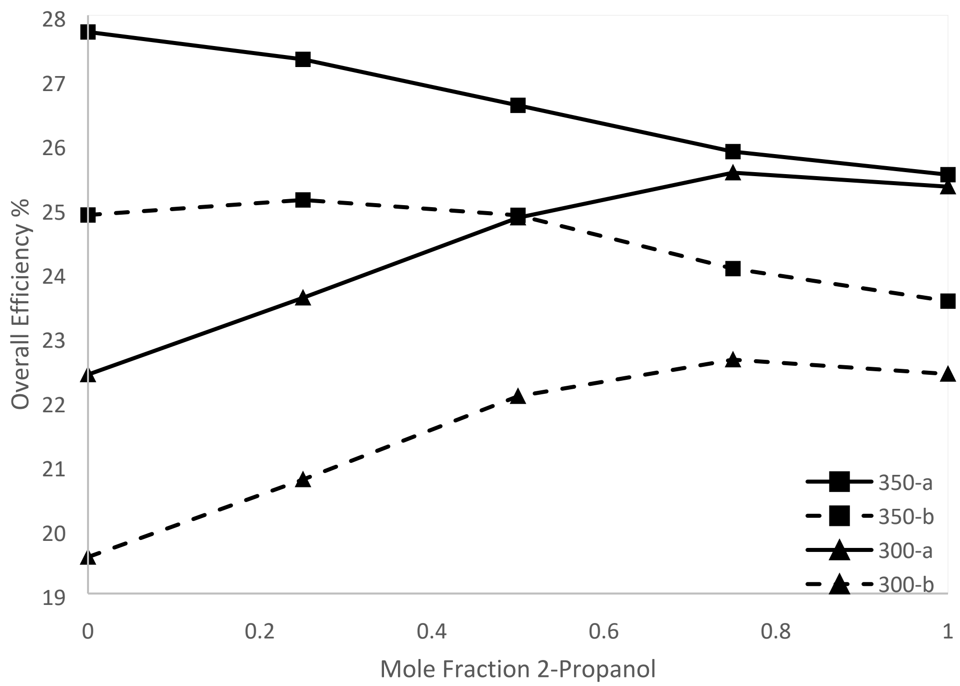

Fig. 11. Effect of boundary conditions on the performance of zeotropic mixture for two different heat source temperatures and two different condensation conditions, solid lines for condensation condition a, dashed lines for condensation condition b.

5.4. Economic result

The specific investment costs (SICs) for ORCs using selected fluids working under the 350°C of the source are depicted in Fig. 12 to provide an overview of the economic feasibility of these working fluids. High investment costs and poor performance rule out 1-butanol from this comparison. Propanol (+IHE), 55%P/45%W, and 75%P/25%B (+IHE) result in the lowest SICs with values between 4,100 and 4,600 €/kW for atmospheric condensation scenario. While for cycles with sub-atmospheric condensation pressure, toluene (+IHE), 70%P/30%W, and MM (+IHE) show the lowest SICs with values among 3,394 to 4,866 €/kW.

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Total investment costs are higher for sub-atmospheric condensation scenario compared to cycles with atmospheric condensation. This rise in values is predictable since the plant capacity increases with the decrease of condensation pressure, so the size of the components increases and results in higher overall costs. Propanol and its mixture with water or butanol do not show an improved economic result for sub-atmospheric condensation. These fluids result in higher SICs, which means the rate of increase in power output is less than the rate of increase in the investment cost. While toluene and MM in a recuperated cycle show lower specific investment costs. The higher total investment cost is overcompensated with a significant increase in power output. Therefore, these fluids are more appropriate for ORCs with lower condensation pressures.

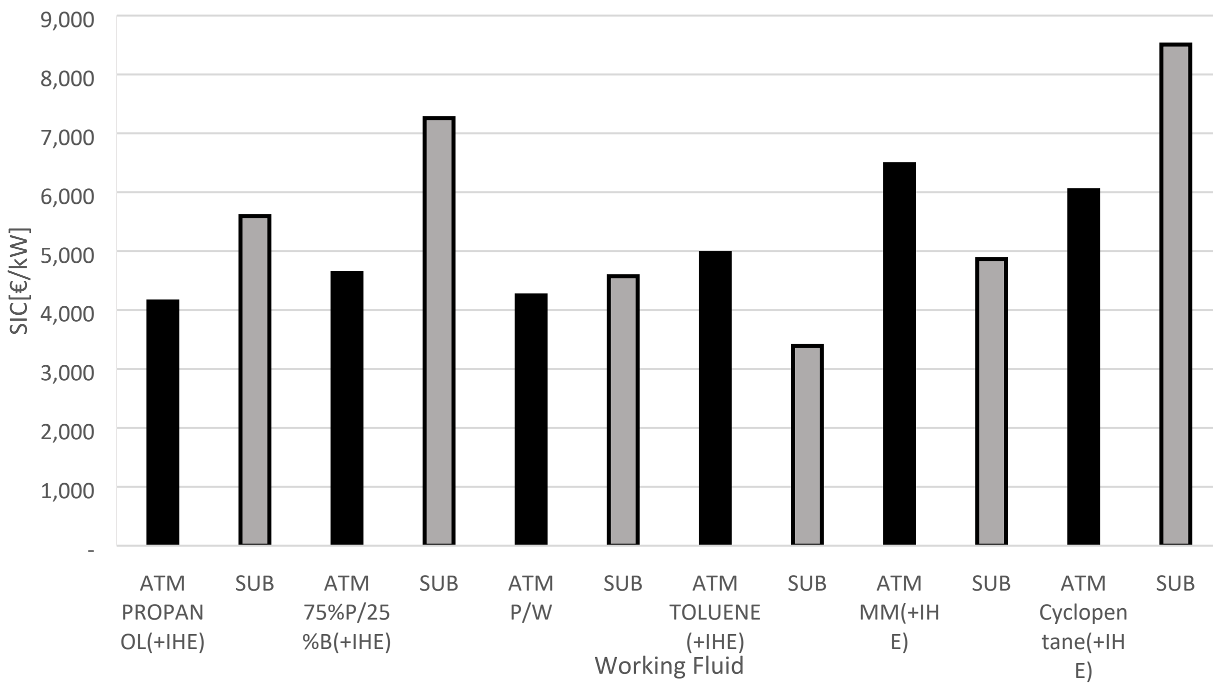

Fig. 12. Specific investment cost using APEA for selected working fluids under the 350°C of the heat source with atmospheric condensation (black bars) and sub-atmospheric condensation (gray bars) pressures.

For all the fluids under this study except for MM, the evaporator is the most expensive module component (more than 50% of the total cost and even more). In the case of MM, the recuperator cost is comparable to the evaporator cost due to the high duty of the IHE for this working fluid. Recovering heat from hot air at atmospheric pressure and considering a lower cooling limit temperature for heat carrier (lower LMTD and the consequently larger area of hat exchanging) lead to more expensive evaporators and higher SICs. Comparing with the available data, the result in this work is higher or, for the best cases, agrees with the upper range of the specific investment costs reported in [35, 44, 45]. Some authors considered an intermediate loop in their heat recovery cycle,

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so the cost for evaporators significantly decreases. However, they did not include the cost of the primary heat exchanger, which recovers heat from flue gases or hot air, in their calculated SICs. Also, it should be recalled that in this work, the cycles are thermodynamically optimized to maximize the power output, and in general, these cycles are not equivalent to economically optimized cycles.

6. Conclusions

This work dealt with the techno-economic assessment of the 2-propanol/1-butanol zeotropic mixture and the 2-propanol/water azeotropic mixture as a working fluid in ORCs for waste heat recovery applications. Toluene, MM, and cyclopentane as common working fluids in commercial ORCs were included to provide a comparison. The P/W mixtures with compositions near the azeotropic point and P/B mixtures rich in propanol resulted in higher overall efficiencies with respect to the commercial working fluids. Only cyclopentane performed better when atmospheric condensation was assumed. Lower SIC values were found for the 65%P/35%W and 75%P/25%B mixtures compared to toluene, MM, and cyclopentane in ORCs with atmospheric condensation pressures. Also, the mixture of 70%P/30%W showed the best economic performance after toluene for the sub-atmospheric condensation scenario.

The superior performance of zeotropic mixtures over the most efficient pure fluid in the mixture was not found in this study. The boundary conditions considered for condensation were the main reason for the lower overall efficiency of P/B zeotropic mixtures than pure propanol. The benefit of the zeotropic mixture was detected when the condensation pressure was not assumed as a fixed value for different compositions and a 10°C temperature glide in cooling air was added to boundary conditions. However, the gain in overall efficiency using a suitable composition, that provides the best temperature profiles matching in the condenser was only 1%.

Considering different aspects of the studied working fluids, the following conclusions are reached:

- Propanol/butanol mixtures rich in propanol and propanol/water mixtures with compositions near azeotropic points with sub-atmospheric condensation can deliver 15-30% higher net power compared to commercial fluids considered in this work for heat source temperatures between 250-350°C.
- For atmospheric condensation, the mixtures perform superiorly compared to toluene and MM, with higher overall efficiency in the range of 45-75%.
- Cyclopentane performs better in cycles with atmospheric condensation, while toluene and MM lead to poor performance in this scenario.

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- The superior performance of the zeotropic mixtures over the most efficient pure fluid in the mixture totally depends on the considered boundary conditions.
- Based on economic analysis, the mixtures under this study can lead to the lowest SIC values for atmospheric condensation.
- Propanol/water mixtures may be preferred over propanol/butanol mixtures due to their superior thermodynamic (14% higher W_{NET} for 350°C of the heat source) and economic performance (9% smaller SIC) lower flammability hazard.
- A negative point about the mixtures under this study, besides their flammability issues, is high working pressures.

Finally, it can be noted that other economic parameters such as the cost of electricity, internal rate of return, payback time, and NPV should be applied to provide a more analytical overview. On one side, the lack of experimental data for thermodynamic models in high pressures brings up a considerable amount of uncertainty in predicting the cycle behavior. Providing the necessary data in the future can lead to more accurate simulations. On the other side, predicting the heat transfer properties of mixtures is a complicated task that needs more research to lead to more reliable results. Moreover, an updated cost reference, which is specifically designed for ORC applications, is needed in the open literature to provide a more realistic economic assessment with smaller deviations from real projects.

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