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INCREASING THE EFFICIENCY AND GENERATED ELECTRICITY OF ORGANIC RANKINE CYCLES BY USING ZEOTROPIC MIXTURES AS WORKING FLUIDS

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ABSTRACT

We present a systematic and comparative study of the potential of zeotropic mixtures as working fluids in ORCs, considering most of the commonly used hydrocarbon and siloxane substances as components in various concentrations. We investigate the impact on the operation, the efficiency and power output of an ORC. The ORC cycle is realistically simulated in steady state conditions, taking into account all elements of an actual cycle (including an internal heat exchanger). By performing a pinch analysis, the power output is maximized, given the heat profiles of both the heat source and heat sink. The use of suitable zeotropic mixtures as working fluids has a positive effect on the ORC performance in all investigated cases. The potential increase in cycle efficiency and generated electricity is larger for lower temperature heat sources and when the temperature drop over the heat source exchanger is larger. When the ORC is optimized for operation with a low temperature heat source, the potential for increase in electricity production (maximum reported value approximately 23%) by using mixtures is particularly remarkable.

INTRODUCTION

In the last several years, in a context of rising electricity demand and cost, the generation of power from industrial waste heat and geothermal or solar sources has attracted an increasing amount of attention. The organic Rankine cycle (ORC) [1] is a viable answer, when dealing with heat sources at low temperature levels, i.e., below 300 °C.

The total efficiency of a Rankine cycle [1] is a function of the temperatures of the heat source and sink, the performances of the cycle components, and the thermophysical properties of the working fluid. Until recently, only pure fluids, i.e., consisting of a single chemical substance, were considered as the operating medium of ORC installations [2–21].

Possibly the largest shortcoming of a pure fluid in its application in an ORC, is the fact that the evaporation and condensation processes occur isothermally. As a result, the tilted temperature profiles of the heat source and sink cannot be approximated sufficiently well by the temperature profiles of the fluid in the evaporator and condenser stages, which leads to large irreversibilities. The use of mixtures of properly chosen components as the ORC medium can partially resolve this problem.

Zeotropic mixtures, on the other hand, are characterized by non-isothermal phase transitions at constant pressure. These fluids are excellent candidates to match the heat source and sink profiles and hence reduce the irreversibilities, promising a better cycle performance. The potential of mixtures – and their non-isothermal phase transitions – is already exploited in cryogenic refrigeration, where they are at the basis of improved cooling performance [22].

Only a few studies on the use of mixtures as ORC working fluids have been published. In the domain of hydrocarbon mixtures, Li et al. [23] compared the cycle efficiency of R141b/RC318 mixtures with that of three pure fluids. It was found that the use of mixtures makes a wider selection of working fluids possible. The increase in thermal and exergy efficiency by adding a recuperator was higher for the mixture R141b/RC318 than for R141b. For a low temperature solar ORC, Wang et al. [24] compared three different mixture compositions of dry R245fa and wet R152a to pure R245fa, in a range from 25 °C (condensation temperature) to 85 °C (vaporization temperature). The main benefits of the mixtures were that the cost of the cycle could be reduced as smaller expanders were possible and that the range of usable fluids increased. In an experimental study of a low temperature ORC by the same authors [25], solar collector efficiencies and overall efficiencies of zeotropic R245fa/R152a mixtures were found to be higher than for pure R245fa. An increase of up to

29.1% in energy production by using the mixtures was observed. Heberle et al. [26] performed detailed simulations for isobutane/isopentane and R227ea/R245fa mixtures to investigate the exergy efficiency. It was shown that for a heat source temperature below 120 °C, the efficiency increase can reach 15%. Mixtures of either hydrocarbons or siloxanes were investigated by Angelino and Colonna [27]. For multicomponent mixtures, enhanced performance was observed, as the cooling device required less power.

Still, the research into zeotropic mixtures is limited and mainly concerned with specific cases. In this paper, we present a systematic and comparative study of the potential of zeotropic mixtures as working fluids in ORCs, considering several of the commonly used hydrocarbon and siloxane substances as components in various concentrations. We investigate the impact on the operation and efficiency of an ORC, using a purposely designed tool that takes into account all elements of an actual cycle. Two types of heat source are considered, at temperature levels corresponding to a typical geothermal source and to a flue gas source. We include an optimization of the recuperated heat, which yields upper bounds for the electricity production.

CYCLE

The ORC installation that is considered in this study is schematically represented in Fig. 1. The pump (Fig. 1, no. 1) pressurizes the ORC medium, which is then lead through the internal heat exchanger (no. 2, also known as recuperator), where it can absorb heat that is recovered from the stage after expansion. Next, in the evaporator (no. 3), the heat source brings the fluid to its evaporation point, turning it into vapor. Operational pressures and related fluid temperatures depend on the temperature of the heat source, specified at in- and outlet of the heat exchanger. Saturated and related fluid temperatures depend on the temperature of the heat source, specified at in- and outlet of the heat exchanger. Saturated vapor then enters the turbine (no. 4) and expands there to a superheated vapor, while delivering work that is used to generate electricity (no. 5). Finally, after being passed through the recuperator, the medium is condensed again to the liquid state in the condenser (no. 6) using a specified heat sink. The included recuperator (no. 2) is a regularly used component to increase the performance of an ORC. The effectivity of the recuperator is specified by the temperature difference ΔT_{recup} between the fluid entering the condenser and the fluid coming from the pump.

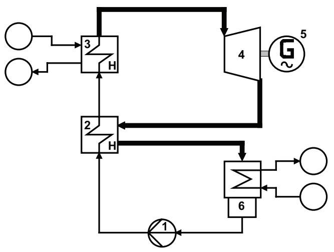

Figure 1 Cycle diagram of the ORC, including a recuperator. Indicated are (1) pump, (2) recuperator, (3) evaporator, (4) turbine, (5) generator, and (6) condenser.

To analyze the influence of the heat source temperature level on the applicability and potential of different fluid mixtures, we modelled two heat source types. The first is a low temperature heat source, perhaps representing a geothermal well. The heat source medium (in this case, water) enters the counterflow type heat exchanger at a temperature of 150 °C and exits the heat exchanger at 135 °C, as heat is transferred from this medium to the ORC fluid for its evaporation. In general, the amount of transferred heat depends on the type and mass flow of the heat source medium, the ORC medium, and the heat exchanger design, and is fixed here at 966 kW. The corresponding cycle conditions are given in Table 1. The second type of heat source, possibly representing a flue gas heat source, has a higher temperature and provides 1287 kW of thermal power. The temperature gradient over the heat exchanger is from 250 °C to 200 °C. Its cycle is described by the parameters in Table 2.

Note that the same component efficiencies are chosen for the two heat source types, to enable an objective comparison. In reality, an ORC applied to a higher temperature heat source often has a turbine with a dedicated design, with isentropic efficiencies of 75% or more. Later in this paper, the heat source temperatures will be varied to further investigate their influence on the applicability and potential of predefined mixtures.

Heat source	Inlet temperature	150 °C
	Outlet temperature	135 °C
	Mass flow	15 kg/s
Heat sink	Inlet temperature	25 °C
	Outlet temperature	35 °C
Cycle	Isentropic pump efficiency	80 %
	Isentropic turbine efficiency	65 %
	Generator efficiency	97 %
	Pinch evaporator	20 °C
	Pinch condenser	10 °C
	ΔT_{recup}	15 °C

Table 1 Parameters for the low temperature heat source, corresponding heat sink and applied ORC. The heat source is water at 5 bar. The heat sink is water at 4 bar.

Heat source	Inlet temperature	250 °C
	Outlet temperature	200 °C
	Mass flow	25 kg/s
Heat sink	Inlet temperature	35 °C
	Outlet temperature	50 °C
Cycle	Isentropic pump efficiency	80 %
	Isentropic turbine efficiency	65 %
	Generator efficiency	97 %
	Pinch evaporator	30 °C
	Pinch condenser	20 °C
	ΔT_{recup}	20 °C

Table 2 Parameters for the high temperature heat source, corresponding heat sink and ORC. The heat source is air at 1 bar. The heat sink is water at 5 bar.

Medium	C [mole frac.]	p_{evap} [bar]	p_{cond} [bar]	p_{ratio}	$\dot{m}$ [kg/s]	P_{pump} [kW]	P_{gen} [kW]	η_{cycle} [%]
isobutane	1	30.8	5.9	5.2	2.59	−15.3	98.1	8.58
R245fa	1	20.3	2.9	7.1	4.47	−7.5	100.3	9.61
isopentane	1	11.0	1.7	6.4	2.40	−4.7	105.0	10.38
R365mfc	1	9.4	1.2	8.1	4.25	−3.6	104.1	10.40
pentane	1	9.2	1.3	6.9	2.27	−3.7	104.9	10.48
cyclopentane	1	6.5	0.9	7.5	2.08	−2.0	104.7	10.63
isohexane	1	4.9	0.6	8.3	2.40	−2.0	105.6	10.73
toluene	1	1.3	0.1	13.1	2.04	−0.4	105.2	10.86
Solkatherm	1	9.7	1.3	7.3	5.70	−4.3	106.4	10.58
R245fa-R365mfc	0.30-0.70	13.1	1.5	8.7	4.28	−5.0	109.5	10.82
R245fa-isopentane	0.20-0.80	14.7	2.0	7.2	2.83	−6.3	110.8	10.82
isobutane-isopentane	0.26-0.74	15.3	2.2	7.0	2.38	−6.6	112.8	10.99
R245fa-pentane	0.24-0.76	13.3	1.7	8.0	2.78	−5.4	112.7	11.12
isopentane-isohexane	0.43-0.57	7.6	0.9	8.8	2.35	−3.2	114.2	11.49
pentane-hexane	0.50-0.50	6.4	0.7	9.5	2.22	−2.6	114.1	11.55
isopentane-cyclohexane	0.79-0.21	9.1	1.1	8.2	2.29	−3.6	115.3	11.57
isopentane-hexane	0.61-0.39	8.1	0.9	8.8	2.29	−3.3	115.1	11.58
R245fa-isopentane-isohexane	0.05-0.64-0.31	10.0	1.2	8.4	2.45	−4.2	115.5	11.52
R245fa-pentane-hexane	0.01-0.52-0.47	6.8	0.7	9.7	2.23	−2.7	115.4	11.67
isopentane-isohexane-cyclohexane	0.11-0.44-0.45	4.7	0.4	10.5	2.22	−1.7	115.1	11.74

Table 3 Simulation results for the ORC applied to the low temperature heat source. Listed are the ORC medium composition, optimal concentrations, and corresponding evaporation pressure, condensation pressure, pressure ratio, medium mass flow rate, pump power, generator power, and cycle efficiency.

SIMULATION AND ASSUMPTIONS

We developed a tool to simulate the described cycle. The FluidProp library [30], in combination with the REFPROP 8.0 database [28], provided the thermophysical data of the considered mixtures and pure fluids. Central in our calculations is a pinch analysis [30] of the heat flows. A nonlinear optimization algorithm enables the determination of the maximal power output and corresponding operating pressures with respect to the preset pinch temperatures. The same algorithm can be used to find the mixture composition that maximizes the cycle efficiency. We define the cycle efficiency as the ratio of the net output power (electricity produced by the generator at the turbine minus the consumed electricity by the pump) over the thermal input power (source heat transferred to the ORC medium in the evaporator). Furthermore, the tool offers the possibility to analyze the temperature profiles in the evaporator, condenser and recuperator.

The performance of the cycle is evaluated assuming steady state conditions of all components, described by constant values for the parameters (see Tables 1 and 2). We also assume that no pressure or heat losses occur between cycle components and that mass and energy are conserved in each cycle component. The temperatures and pressures of the ORC medium are determined by the heat source and sink temperature profiles, offset by preset pinch temperatures, which are defined as the minimum temperature differences over the heat exchangers. Our study focuses on the overall cycle performance, rather than on the optimization of individual cycle components (i.e. the heat exchangers, turbine and pump). This pinch methodology ensures an objective thermodynamic comparison, based solely on the differences in fluid properties.

RESULTS AND DISCUSSION

First we report and discuss the results for all considered mixtures for the heat sources characterized by the parameters in Tables 1 and 2. Then we extend the analysis with varying temperature gradients and examine the optimization of the electricity production.

Mixture comparison

The results for the examined fluids, suitable for a lower temperature heat source (T_{in} = 150 °C, T_{out} = 135 °C), are presented in Table 3. For comparison, several single component fluids are included. In the second column of Table 3, the mole fraction concentrations that correspond with the highest cycle efficiencies, according to the procedure described in Section 5.1, are listed. Optimal binary mixtures show a 5.6-10.0% increase in generated electric power and a 4.2-11.5% increase in cycle efficiency with respect to their pure constituents. Compared with the binary mixtures, three-component mixtures only yield a small additional increase in generated electric power and efficiency.

The mixture isopentane/isohexane (0.43/0.57) gives a cycle efficiency of 11.49% (compared to 10.38% for isopentane, representing a relative performance increase of 10.7%). The generated electricity for the mixture (114.2 kW) is also substantially higher than for pure isopentane (105.0 kW, an increase of 8.8%). Adding a third component, to obtain the mixture isopentane/isohexane/cyclohexane, results in an efficiency of 11.74% and an electricity production of 115.1 kW (respectively an extra increase of 2.2% and 0.8% compared to the two-component mixture).

Medium	C [mole frac.]	p_{evap} [bar]	p_{cond} [bar]	p_{ratio}	$\dot{m}$ [kg/s]	P_{pump} [kW]	P_{gen} [kW]	η_{cycle} [%]
cyclopentane	1	25.9	1.85	14.0	2.72	−11.7	189.6	13.81
HMDS	1	9.1	0.35	25.9	4.51	−6.9	190.7	14.28
cyclohexane	1	12.0	0.70	17.2	2.76	−5.3	190.7	14.40
OMTS	1	2.7	0.05	50.6	5.01	−2.1	187.5	14.40
toluene	1	6.2	0.26	23.5	2.64	−2.4	188.7	14.48
toluene-cyclohexane	0.6-0.4	8.9	0.38	23.5	2.68	−3.6	197.9	15.09
HMDS-OMTS	0.7-0.3	6.5	0.18	35.3	4.73	−5.2	200.9	15.20

Table 4 Simulation results for the ORC applied to the high temperature heat source. Listed are the ORC medium composition, optimal concentrations, and corresponding evaporation pressure, condensation pressure, pressure ratio, medium mass flow rate, pump power, generator power, and cycle efficiency.

Considering now another example, when hexane is added to pure pentane to create the mixture pentane/hexane (0.5/0.5), an efficiency increase of 10.2% and an increase in generated electricity of 8.8% (up to 114.1 kW from 104.9 kW for pure pentane) is observed. With the addition of R245fa as a third component, an increase of efficiency and generated electricity of only 1.0% and 1.1%, respectively, can be noticed. Note that also in comparison with the azeotropic mixture Solkatherm, a substantial increase in the ORC performance can be achieved by using zeotropic mixtures.

For the higher temperature heat source (T_{in} = 250 °C, T_{out} = 200 °C), with corresponding cycle parameters as in Table 2, our simulation results for compatible single fluids and mixtures are listed in Table 4. Also here, we observe an increase in the generated electric power and cycle efficiency by using mixtures instead of pure fluids. For instance, the specified ORC with the pure siloxane fluid hexamethyldisiloxane (HMDS) as its medium, can generate 190.7 kW of electricity with a cycle efficiency of 14.3%. When another siloxane component, octamethyltrisiloxane (OMTS), is added to create a mixture 0.7/0.3 HMDS/OMTS, an electricity production of 200.9 kW and a cycle efficiency of 15.2% are found, an increase of 5.3% and 6.4%, respectively. Similarly, if the hydrocarbon mixture toluene/cyclohexane (0.6/0.4) is considered for a cycle with parameters as in Table 2, 197.9 kW of electricity can be produced with an efficiency of 15.1%. Compared to the same cycle using pure toluene (generating 188.7 kW with 14.5% efficiency), this represents a power production increase of 4.8% and an efficiency increase of 4.2%.

The electricity production and efficiency improvements, as a result of using mixtures instead of pure fluids, are smaller for the higher temperature heat source model than for the lower temperature heat source model.

Influence of the heat source temperature profile

Previously, only two sets of inlet and outlet temperatures (T_{in} , T_{out}) of the heat source were considered. (See Table 1 for the values of a typical lower temperature heat source and Table 2 for a higher temperature heat source). Here, the effect of a variation of the heat source inlet temperature T_{in} , and of the temperature gradient $\Delta T_{src} = T_{in} - T_{out}$ over the heat exchanger is investigated. This temperature gradient is directly related to the thermal power recuperated from the heat source. The heat sink and cycle parameters are kept constant as in Table 1 and 2.

For the low temperature heat source, with a 0.5/0.5 mixture of pentane/hexane as the working fluid, the cycle efficiency increase (with respect to pure pentane) as a function of ΔT_{src} is illustrated in Fig. 2(a), for several values of T_{in}. We note, first, that the efficiency increase is higher when the inlet temperature T_{in} of the heat source is lower. Secondly, the efficiency increase is also higher when the temperature drop ΔT_{src} over the heat exchanger is higher, i.e., when the outlet temperature T_{out} decreases. The same observations [Fig. 2(b)] can be made for a toluene/cyclohexane mixture as the working fluid in an ORC operating with the higher temperature heat source, but not for siloxane mixtures [Fig. 2(c)]. Except for very dry fluids such as

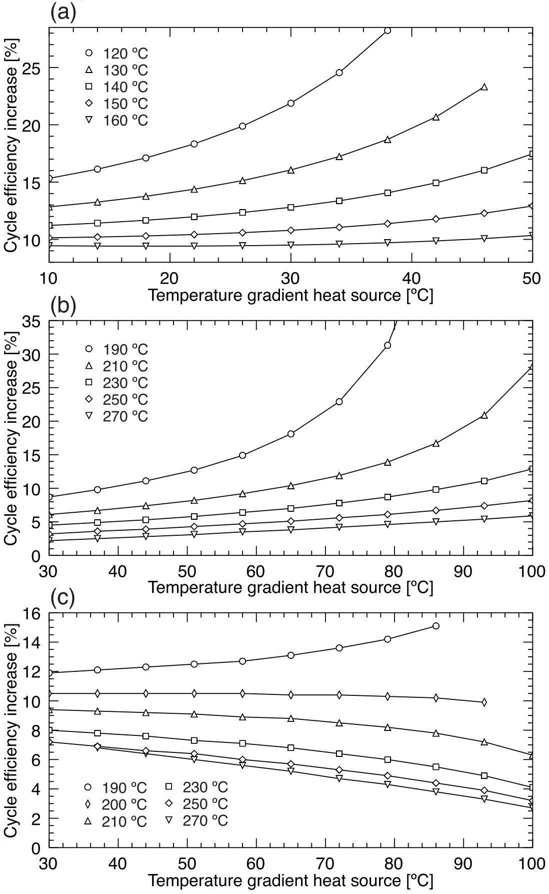

Figure 2 Cycle efficiency increase as a function of the heat source temperature gradient over the evaporator for (a) 0.5/0.5 pentane/hexane compared to pure pentane, (b) 0.6/0.4 toluene/cyclohexane compared to pure toluene, and (c) 0.7/0.3 HMDS/OMTS compared to pure HMDS. Heat source temperatures are depicted in the legend. Other parameters as in Table 1 (a) and Table 2 (b,c).

siloxanes, the benefit of using a mixture for heat sources with the considered parameters and inlet temperatures, increases when the temperature difference between the inlet and outlet of the heat exchanger is larger.

Bear in mind, however, that the cycle efficiency in absolute terms decreases with increasing ΔT_{src}. The production of electricity, on the other hand, increases with ΔT_{src} until it reaches a maximum at ΔT_{opt} , and then decreases with ΔT_{src}. The generated electricity, rather than the overall cycle efficiency, will in most cases be the most relevant factor in the optimization of an ORC. The higher relative increase in electricity production of a mixture, compared to the corresponding pure fluid, for higher ΔT_{src}, makes mixtures as the working fluid additionally promising, in particular for the ΔT_{opt} that yields maximum production.

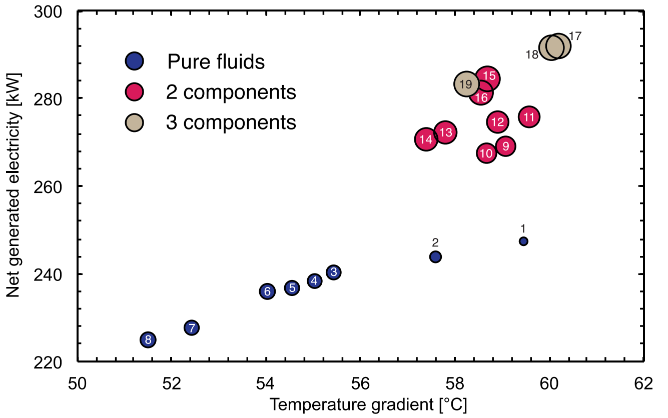

Figure 3 Maximum net generated electricity versus corresponding optimal heat source temperature gradient for the fluids and mixtures given in Table 5, with optimal mixture compositions. Disk radius is proportional to the relative cycle efficiency. The heat source is at 150 °C, other parameters as in Table 1.

For a heat source at 150 °C, the maximum net generated electricity versus the corresponding temperature gradient ΔT_{opt} for all considered pure fluids and mixtures is plotted in Fig. 3. The mixture compositions are also optimal. The radius of a disk symbolizing a data point is proportional to the relative cycle efficiency. This figure clearly visualizes the increased electricity production potential of mixtures compared to pure fluids. The mixtures operate optimally at higher ΔT_{opt} compared to pure fluids, signifying an increase in recuperated power from the heat source. In addition, as already mentioned, the evaporation (condensation) process occurs at higher (lower) average temperature, resulting in a higher cycle efficiency. For the considered heat source and ORC, under optimal operation, an increase in electricity production of over 23% by using mixtures instead of pure fluids as medium is attainable. Again, 3-component mixtures only yield a minor increase in generated electricity compared to 2-component mixtures. In our survey, using R245fa/isopentane/isohexane (0.64/0.17/0.19) leads to the highest net electricity production (291.8 kW).

No.	Fluid	C [mole frac.]	η_{cycle} [%]
1	isobutane	1	6.6
2	R245fa	1	6.7
3	R365mfc	1	6.8
4	isopentane	1	6.8
5	pentane	1	6.8
6	isohexane	1	6.9
7	cyclopentane	1	6.8
8	toluene	1	6.9
9	R245fa-R365mfc	0.41-0.59	7.2
10	R245fa-isopentane	0.28-0.72	7.2
11	isobutane-isopentane	0.74-0.26	7.3
12	R245fa-pentane	0.32-0.68	7.3
13	isopentane-isohexane	0.47-0.53	7.4
14	pentane-hexane	0.54-0.46	7.4
15	isopentane-cyclohexane	0.87-0.13	7.6
16	isopentane-hexane	0.75-0.25	7.6
17	R245fa-isopentane-isohexane	0.64-0.17-0.19	7.6
18	R245fa-pentane-hexane	0.61-0.30-0.09	7.6
19	isopentane-isohexane-cyclohexane	0.80-0.09-0.11	7.7

Table 5 Simulation results for the ORC applied to the low temperature heat source for maximum achievable energy production. Listed are the medium numbers corresponding to Fig. 8, medium composition, optimal concentration, and cycle efficiency.

CONCLUSIONS AND FINAL REMARKS

In summary, the use of suitable zeotropic mixtures as working fluids has a positive effect on the ORC performance in all investigated cases. An increase in cycle efficiency, for binary mixtures, of 11.5% and an increase in generated electricity of 10.0% is found possible for heat source and ORC cycle parameters typical for a geothermal source (150 °C). The potential for efficiency and electricity production increase is less pronounced (6.4% and 5.3%, respectively) for a heat source type with parameters corresponding to a flue gas source (250 °C). In the considered cases, the addition of a third component to a binary mixture has only a small effect. The potential increase in cycle efficiency and generated electricity is larger for lower temperature heat sources and when the temperature drop over the heat source exchanger is larger. When the ORC is optimized for operation with a low temperature heat source, the increase in electricity production (approximately 23%) by using mixtures is particularly remarkable. The presented study was performed with an optimization tool that automatically selects the optimal pressures, mass flows and medium temperatures of the ORC under various assumptions. In reality, circumstances may prevent achieving these optimal settings. Also, the inner workings of the components (especially of the heat exchangers, but also of the pumps and turbine) and their optimization for mixtures as a medium, was not taken into account. The accuracy of the results can be further improved by considering the variation of the heat transfer coefficient of the mixture along the length of the heat exchangers. Notwithstanding the potential beneficial effect on the efficiency and electricity production, the use of mixtures also has some disadvantages. Leakages present a larger problem than is the case for pure fluids, especially in the evaporation stage. Some mixtures are patented, barring their use or incurring an extra cost. Nevertheless, the presented results demonstrate the potential for increased ORC performance by using mixtures, especially for low grade heat sources, if proper consideration is given to their selection. It is for the user to offset the increased performance against a higher installation complexity and cost and to incorporate the environmental impact of the fluids.

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