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Research Article

Organic rankine cycle systems with mixture of pure fluids: On infeasible fluid's fractions due to the interaction between the mixture glide and the hexs pinchs

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ABSTRACT

The Organic Rankine Cycle (ORC) is a promising technology for power generation from low-grade heat. The selection of working fluids is one of the important key points to improve the performance of an ORC system. Zeotropic mixtures show promising performances as working fluids. In fact, their temperature glide during phase change enables better match between the working fluid and the heat source/sink temperatures. In order to reveal the performance of mixture in ORC system, this paper deals with the thermodynamic model of the subcritical Organic Rankine Cycle (ORC) systems driven by low grade heat source while using zeotropic mixture working fluids with a special consideration to the interaction between phase change glides and the pinch value and their location in both the evaporator and the condenser (HEXs). Zeotropic mixtures of seven pure fluids are evaluated as working fluids for a subcritical ORC system. The mass fraction effects of mixtures on the thermal efficiency are analyzed. For given working conditions (working fluid mass flow, pressure and bubble temperature) the results show that for each considered zeotropic mixture there exist mass fraction ranges that are not consistent with the pinch values constraint in the HEXs and leads to so-called 'infeasible zones' with unreal HEXs dimensions. Results shows also that, out of these "infeasible fractions" zone, keeping unchanged the working conditions, the thermal performances of ORC system using zeotropic mixture are always better than the thermal performances of the same systems using the correspondent pure fluids. In addition, out of these highlighted "unfeasible zones" it was found that mixture with high temperature glide improve the thermal efficiency of ORC system.

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INTRODUCTION

Following the energy shortage and the related environmental pollution problems that have become more serious in recent years, the use of low temperature energy has attracted attention around the world [1, 2]. In fact, renewable energy resources, such as solar or geothermal, often stand as low temperature energy. The industrial heat waste stand also mainly as low temperature energy in the range of 60–250°C. Among the used technologies for heat power conversion for this temperature range, the Organic Rankine Cycle (ORC) systems appear to be the best approved [3–6].

Organic Rankine Cycle has the same system configuration as steam Rankine Cycle but uses organic fluids as the working fluid instead of water [2, 3]. The mean reason is that the performance of this thermodynamic cycle is better with organic fluids when the heat source is a low-grade energy [7]. However, for giving source and sink temperatures, its performances depend on the convenience choose of the working fluid. There are two main working conditions of the heat exchangers (HEXs) of the ORC system's that directly affect the whole performances of the system. The first is the "pinch" which is the minimum temperature difference between the fluids in each HEX; the second is the entropy generation in the HEX related to the fluids temperature difference. In fact, the lower are the pinchs [8], the higher are the heat exchangers sizes and costs because of the bigger heat exchange surfaces needed in this case. Conversely, the biggest are the pinchs, the lower are the system performances because of the highest entropy generation due to the fluid's temperature difference. Nevertheless, the pinch had to be maintained above an imposed minimal value in each HEX in order to ensure the heat flow between the fluids with acceptable exchange surfaces sizes. Taking into account this tradeoff between these working conditions in connection with the use of zeotropic mixture as working fluid, one had to find the working conditions that permits the best thermodynamic and thermo economic performances of the system.

In the case of pure fluid assuming a single phase heating/cooling fluid, the HEX's pinch may stand [9] at the working fluid bubble or dew point depending on the respective fluids mass flows and heat capacity. The pure fluid constant temperature phase change in the HEXs increases its temperature gap with the heating/cooling monophasic fluid along the evaporator/condenser and leads to high entropy generation [10]. Using zeotropic mixtures as working fluids seems to be a viable option to reduce the entropy generation in the HEXs thanks to their non-isothermal phase change process [11–13]. They present a so-called temperature glide when they perform a constant pressure phase change: for a given pressure, the dew point (i.e the mixture vapor condensing start temperature) and the bubble point (i.e the mixture liquid evaporating start temperature) are different, and the glide is the temperature difference between those two points. It depends on the fluid pressure and consequently its values aren't the same in the evaporator and in the condenser [14, 15]. For the current used working fluid, the glides are in the range 2–20 K [16, 17]. Due to the working fluid phase change temperature glide, the pinch location in both evaporator and condenser can occur at different positions depending on the base fluids (i.e the pure fluids that constitutes the mixture) fractions, and on the system working conditions such as the high and low pressure and the heat and cold fluids inlet temperature in the correspondent HEXs and the fluid's mass flow rate. However, when the working fluid is a zeotropic mixture, the HEXs need [17–19] wider heat transfer area because of the decrease on the fluids temperature difference.

Using zeotropic mixtures as working fluids have gained interest recently by many research in the specialized literature but without special emphasis on the interaction between the working fluid glides and the HEXs pinchs. Kang et al.

[11] studied the effect of 10 zeotropic mixtures on the performance of ORC system. Their results showed that the optimal mass ratio of the base fluids in the mixture that leads to the maximum thermal efficiency corresponds to the maximum temperature glide. Wu et al. [20] investigated first law and second law efficiencies, exergy destruction distributions and the net power output of an ORC system using three zeotropic mixtures as working fluid. They concluded that the better thermal performance is achieved when the cooling water temperature increase in the condenser is nearly equal to the temperature glide of the zeotropic mixture. Shu et al. [21] studied the first and the second law efficiencies of two configurations of ORC systems using mixtures. Their result indicated that the zeotropic mixtures at a certain mixing fraction present better thermodynamic performance than the corresponding pure working fluids. Lecompte et al. [22] analyzed the second law efficiency of an ORC system using seven zeotropic working fluids. They showed that the second law efficiency of mixtures is higher than the one of the corresponding pure working fluids. However, opposite results to the above mentioned ones have been reported by other authors [23–26]. They indicated that mixture fluids don't always lead to better thermodynamic performances compared to their corresponding pure fluids. Such an opposite result was presented by Van long Le et al. [24] who conducted an optimization study of ORC system using n-pentane, R245fa, and their mixtures and found that pure n-pentane shows better optimal performances regarding the exergy efficiency than its zeotropic mixtures with R245f. Feng et al. [23] showed that mixtures lead to bad thermodynamic and economic performances compared to their corresponding pure fluids. Wu et al. [20] indicated that mixtures had lowest economic performance than the corresponding pure fluids. Liu et al. [27] investigated the effect of the dew point temperature of the mixtures at the condenser pressure on the performance of ORC systems. Their work has been conducted under different restrictive conditions in reference to the work of J. Lu et al. [28]. Their results indicated that when the mixture dew point at the condenser pressure is fixed, there is only one optimal working fluid mass fraction that maximizes the thermal efficiency and, simultaneously maximizes the net power output and the exergy efficiency. The work of Li et al. [29] concluded that each mixture presents a range of operating conditions where the corresponding pure fluids perform better. Venkatarathnam et al. [30] investigated the issue of pinch points temperature and glide matching in condensers and evaporators for zeotropic refrigerant mixtures and they developed a simple procedure to find the location of the pinchs in the HEXs.

Regarding the above mentioned recent studies, the use of pure or mixture fluid is still a controversial question in the literature and it seems that there are no systematic studies on the interaction between the zeotropic fluid glide and the pinch location and value, and consequently on the incidence of this interaction on the whole performance of the ORC. Furthermore, one can notice that the comparisons between the performances of the zeotropic mixture and their corresponding pure fluids have been made under different conditions regarding the working fluid's pressure [24]. Besides, among the above-mentioned studies there are some [19, 31] where the authors didn't pay attention to the fact that the glides of their used fluid mixture induce a non-realistic value of the pinch value in their ORC HEXs, and to the fact that despite what they expect their actual pinchs located in the HEXs are too little and sometimes null. Hence, the issue is that, given a fluid's fractions in the mixture, under a given set of working conditions, i.e. the imposed/desired HEXs pinch, the working fluid flow rate, the pressure and the temperature, and the heating fluid mass flow rate and temperature, the temperature glide of mixture fluid leads to decreasing the two fluids temperature difference in the condenser and in the evaporator under the pinch desired value. Since the HEXs are designed under the expected pinch value, this actual pinch issue hugely affects the HEXs performances and hence, the overall ORC system performances.

Although there were many investigations associated with the optimization of the ORC system using zeotropic mixture as working fluids, detailed influence of the pinch temperature difference on the ORC performance was rarely found. Hence, the main objective of this study is to analyze the influences of the pinch temperature difference on the performance of an ORC system for low-grade heat source with different pure working fluids with different critical temperature and their zeotropic mixtures. A comprehensive comparison of their thermodynamic performances is performed using the Refprop® database from NIST for the physical properties of organic used fluids.

In fact, under the same working conditions, due to entropy generation, one had to expect that performances of the zeotropic mixture working fluid shall remain better than those of the correspondent pure fluids if the value and location of the pinch is carefully sought considering the fluid's glide. Using case studies of a standard ORC system with seven pure working fluids and their mixtures at different fractions, the main purpose of the present study is to show that when keeping unchanged the working conditions (i.e the imposed HEXs pinch, the working fluid flow rate, pressure and temperature, and the heating fluid mass flow rate and temperature), and systematically checking that the fluid's temperature difference don't falls under the desired pinchs thorough the HEXs, the thermal performances of ORC system using mixture are always better than the thermal performances of the same systems using the corresponding pure fluids. However, under each working conditions, there may exist "infeasible fractions" of the mixture that leads to pinch value that stands under the imposed values in one or two HEXs.

System Configuration

Figure 1a shows the configuration of the ORC system considered in the present study. It consists of a basic ORC with its four components: evaporator, pump, turbine, and condenser. The heating/cooling fluids are assumed to be single phase fluids. The working fluid (Fig. 1b) in saturated liquid state (1) is pumped to the evaporator (2) and receives energy from heating source fluid to turn into high-temperature and high-pressure saturated steam (3). The fluid is then expanded in the turbine and rotates its shaft. At the outlet of the last (4), the pressure falls to the condensing pressure. Then the steam of the working fluid enters the condenser where it condenses into a saturated liquid state to start a new cycle. The thermodynamic process for the basic ORC system using pure working fluids is illustrated on a temperature-entropy (T- s) diagram shown in Figure 1b. The corresponding temperature-entropy diagram for basic ORC system using zeotropic mixture working fluids is shown in Figure 1c. It appears that due to the zeotropic fluid phase change temperature glide (Fig. 2a); the temperatures differences between the heating/cooling fluid in the evaporator/ condenser and the working fluid are less than in the case of pure fluid. This fact leads to smaller entropy generation. However, larger heat exchange surfaces are needed because of the smallest temperature difference between the fluids in such a way that affects the whole thermo economic performances of the ORC. Notice that for the zeotropic working fluids, one had also to pay special attention to the pinch value to avoid it to go under a chosen limit.

According to the first law, the following equations describe the net power output and the

$$\dot{W}_{net} = \dot{W}_T - \dot{W}_p = \dot{m}_{wf}\ [(h_3 - h_4) - (h_2 - h_1)] \quad (1)$$

$$\eta_{ORC} = \dot{W}_{net}/\dot{Q}_e \quad (2)$$

Where $\dot{m}_{wf}$ represents the mass flow rate of the working fluid.

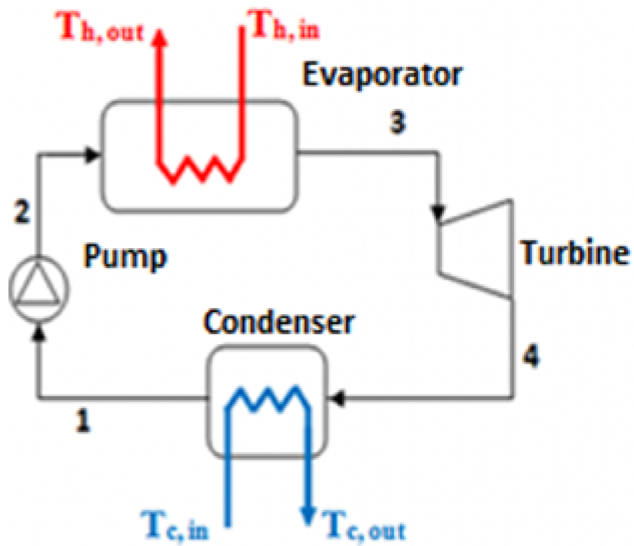

Figure 1.a Schematic diagram of ORC system for low grade heat

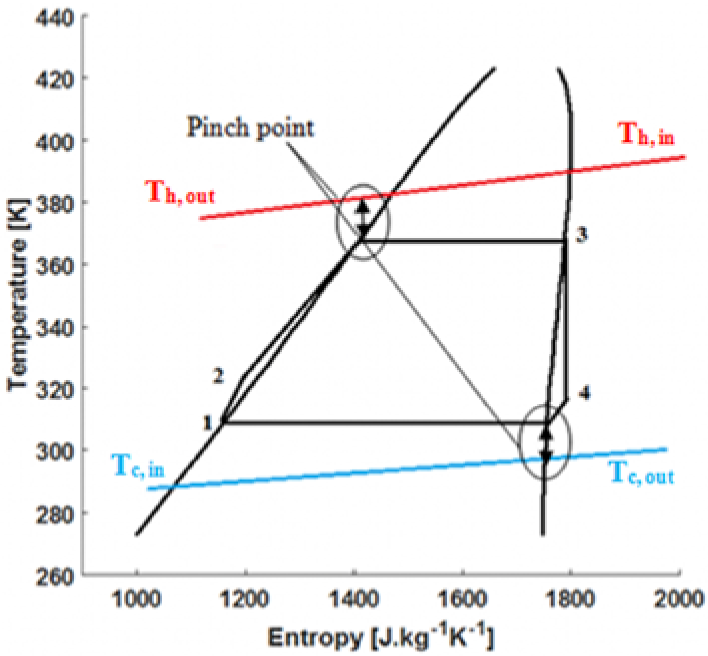

Figure 1.b T– s diagram for ORC system using pure working fluid

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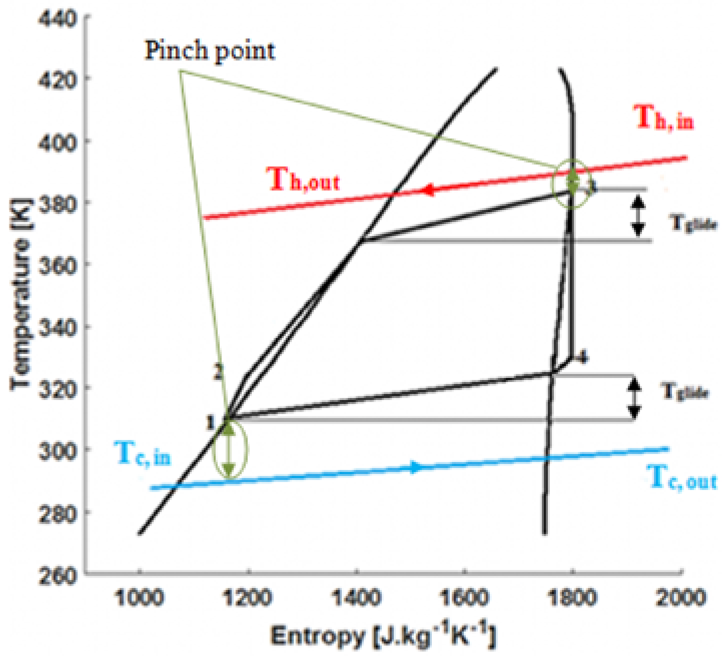

Figure 1.c T– s diagram for ORC system using zeotropic mixture working fluid

THE THERMODYNAMIC PROCESS

Evaporator

The thermodynamic process in the evaporator can be expressed with the following equations:

$$\dot{Q}_e = \dot{m}_h\,(h_{h,in} - h_{h,out}) = \dot{m}_{wf}\,(h_3 - h_2) \qquad (3)$$

$$d\dot{Q}_e = -\,\dot{m}_h\,c_{p,h}\,dT_h \qquad (4)$$

Where $\dot{Q}_e$ is the heat flow rate that the working fluid exchanges in the evaporator, dT_h is the heating fluid temperature drop in the evaporator, and $c_{p,h}$ is the heating water constant pressure specific heat.

In the case of a pure fluid, Figure 1b and Figure 2b shows that the evaporator pinch location (i.e the actual location in the HEX where the minimum temperature difference ΔT_{min} between the fluids happens) stands at the bubble temperature of the working fluid. Notice that in the case of a very low heating fluid mass flow rate, the pinch point occurs at the heating fluid outlet. But in this case it's inlet temperature had to be very high leading to high entropy generation on the evaporator, and hence this configuration is excluded here after. In the case of a mixture (Fig. 1c and Fig. 2c), due to its evaporation glide, the evaporator pinch location may occur at any point between the mixture bubble and dew points at the evaporator pressure (Fig. 2c). Moreover, fixing the base fluids fractions in the mixture, the pinch location and value in the evaporator depends on the ORC system working conditions that are the heating fluid mass flow and inlet temperature, the ORC system high pressure, the working fluid mass flow, the bubble temperature, and the glide at the evaporator pressure.

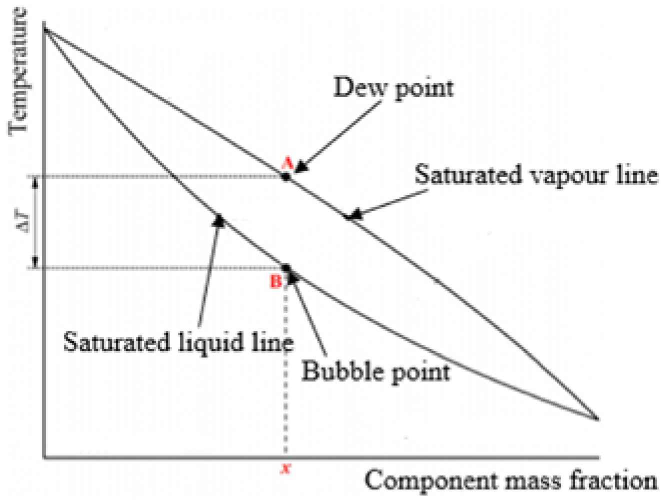

Figure 2.a Dew point and bubble point variation as a function of components mass

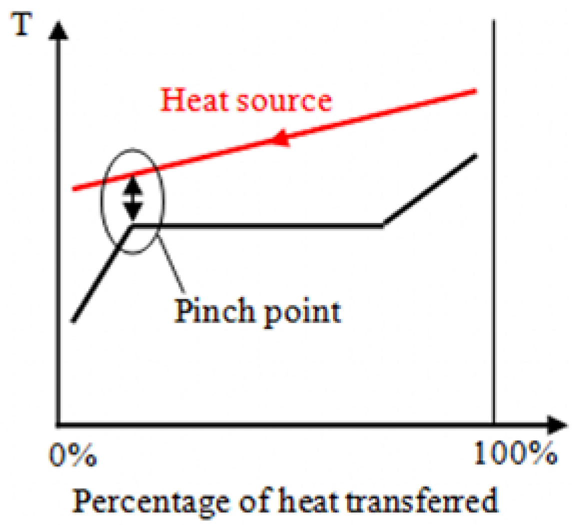

Figure 2.b Streams temperatures profile during the heat addition process in the case of a pure working fluid

Condenser

The thermodynamic process in the condenser can be expressed with equations (5–6).

$$\dot{Q}_c = \dot{m}_c\,(h_{c,out} - h_{c,in}) = \dot{m}_{wf}\,(h_4 - h_1) \quad (5)$$

$$d\dot{Q}_c = \dot{m}_c\, c_{p,c}\, dT_c \quad (6)$$

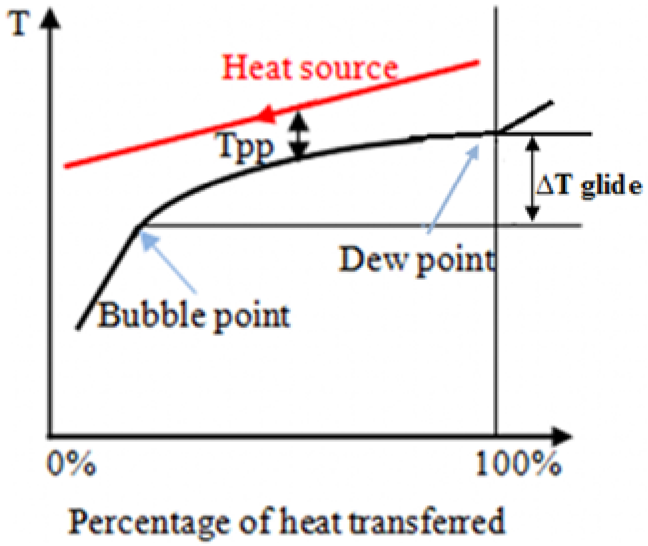

Figure 2.c Streams temperature profile during the heat addition process in the case of a zeotropic mixture

Where $\dot{Q}_c$ is the heat flow that the fluids exchange in the condenser. dT_c is the cooling fluid temperature rise in the condenser and $C_{p,c}$ is the cooling fluid constant pressure specific heat. In the case of a pure working fluid, the pinch location of the condenser happens (Fig. 1b) at the working fluid dew point. In the case of zeotropic mixture, the fluid behaves in the condenser in the same way than in the evaporator: the pinch location may occur in any point between the fluid's dew and bubble points at the condenser pressure. Hence, fixing the base fluids fractions in the mixture, the pinch location and value in the condenser depend on the ORC system working conditions: the cooling fluid mass flow and inlet temperature, the ORC system low pressure, the working fluid mass flow, the dew temperature, and the glide at the condenser pressure.

Turbine and Pump

Assuming that all the ORC system components heat losses to the surrounding environment are negligible, as well as the pressure drops in the connecting tubes, the generated power by the turbine is:

$$\dot{W}_T = \dot{m}_{wf}\,\eta_T\,(h_3 - h_{4s}) = \dot{m}_{wf}\;(h_3 - h_4) \quad (7)$$

Where η_T is the turbine isentropic efficiency, h_3 is the working fluid enthalpy at the evaporator outlet, h_{4s} is the turbine outlet enthalpy for an isentropic expansion process and h_4 is the actual specific working fluid enthalpy at the turbine outlet.

The power consumed by the working fluid feed pump is:

$$\dot{W}_p = \dot{m}_{wf}\,\frac{1}{\eta_p}(h_{2s} - h_1) = \dot{m}_{wf}\;(h_2 - h_1) \quad (8)$$

Where η_p is the pump isentropic efficiency, h_1 is the working fluid enthalpy at the condenser outlet, h_{2s} is the pump outlet enthalpy for an isentropic compression process and h_2 is the actual working fluid specific enthalpy at the pump outlet.

EVAPORATOR AND CONDENSER PINCH LOCATION AND VALUE COMPUTING MODEL

To ensure a realistic dimension for each HEX of the ORC system, one had to put a constraint on the pinch values in the HEXs. This constraint on the pinch value is taken usually in the range 5–20 K. Van long Le et al. [24] take a pinch constraint of 10 K and 5 K in the evaporator and condenser respectively. It's important to find the actual minimum temperature difference ΔT_{min} between the fluids that flow in each HEX and to compare it to the minimal authorized value with respect to the imposed constraint. In an automatized computational procedure aiming to test the performances of an ORC system with a given working fluid, one had to reject each pure or mixture fluids if there is a violation of the constraint on the pinch values in the HEXs.

In the case of a zeotropic mixture, the classical method used to determine ΔT_{min} in the evaporator and the condenser is firstly exposed.

Evaporator Pinch Computing

The evaporator includes three sections: the preheating, the evaporation, and when needed, the superheating process of the working fluid. The current method used for finding the evaporator pinch value had been developed particularly by Qiang Liu and al. [32]. It consists on a discretization of the evaporator process into 20 segments where both the heating and the working fluid temperatures are assumed to be constant. This method is conducted as follows:

For each position $k(1\leq k \leq 20)$ during the evaporation process where the heating fluid is at a temperature $T_{h,k}$ $(T_{h,out} \leq T_{h,k} \leq T_{h,in})$ the exchanged enthalpy rate between the HEX's fluid since the working fluid inlet is given by:

$$\dot{Q}_{e,k} = \dot{m}_{wf}\,(h_{e,k} - h_2) = \dot{m}_h\, c_{p,h}\,(T_{h,k} - T_{h,out}) \quad (9)$$

$h_{e,k}$ is the local specific enthalpy of the working fluid. From equations (3) and (9), the expression of $h_{e,k}$ is:

$$h_{e,k} = \frac{(T_{h,k} - T_{h,out})h_3 + (T_{h,in} - T_{h,k})h_2}{(T_{h,in} - T_{h,out})} \quad (10)$$

The local temperature $T_{e,k}$ of the working fluid in the segment k is then deduced from $h_{e,k}$ thanks to the known properties of the working fluid. The local temperature difference $(T_{h,k} - T_{e,k})$ between the fluids in the evaporator is computed for k=1 to 20. The pinch, which is the minimum value of $(T_{h,k} - T_{e,k})$ is this way found.

Condenser Pinch Computing

The condenser includes two sections: the desuperheating and the condensing process. For an ORC system with a pure working fluid, the condenser pinch location stands at the dew point. In the case of an ORC with a zeotropic mixture working fluid, the pinch location may stand at any position of the condensing process. A similar model to the above exposed one for the evaporator is currently used [16] to determine the pinch location in the condenser: the condenser is divided into 20 segments k where find working fluid and the cooling fluids temperatures are assumed constant. The exchanged enthalpy rate between the HEX's fluid since the working fluid inlet is given by:

$$\dot{Q}_{c,k} = \dot{m}_{wf}\,(h_{c,k} - h_1) = \dot{m}_c\, c_{p,c}\,(T_{cl,k} - T_{cl,in}) \quad (11)$$

$h_{c,k}$ is the local specific enthalpy of the working fluid. From equations (5) and (11), $h_{c,k}$ can be expressed as following:

$$h_{c,k} = \frac{(T_{cl,k} - T_{cl,in})h_4 + (T_{cl,out} - T_{cl,k})h_1}{(T_{cl,out} - T_{cl,in})} \quad (12)$$

The local temperature difference $T_{c,k}$ of the working fluid in the segment k is then deduced form $h_{c,k}$ thanks to the known properties of the working fluid. The local temperature difference $(T_{c,k} - T_{cl,k})$ between the fluids in the condenser is computed for k=1 to 20. The pinch, which is

Table 1. Simulation parameters and boundary conditions used in this study

Item	Parameter	Value
Heat source	Heating water inlet temperature	120°C
	Heating water pressure	5 bars
	Heating water mass flow rate	15 kg/s
Cold source	Cooling water inlet temperature	20°C
	Cooling water pressure	4 bars
Cycle	Working fluid high pressure bubble temperature	90°C
	Working fluid low pressure dew temperature	35°C
	Turbine isentropic efficiency	85%
	Pump isentropic efficiency	70%
	Pinch temperature constraint in the evaporator T_{pinch_e}	10K
	Pinch temperature constraint in the condenser T_{pinch_c}	5K

Table 2. Properties of the studied working fluids [36]

Working fluid	P^{Cr} (MPa)	T^{Cr} (°C)	T^{B} (°C)	ASHRAE 34 Safety Group	ODP	GWP 100 yrs
R245fa	3.64	154.05	15.30	B1	0	1050
R141b	4.21	204.35	32.05	B1	0.11	600
R123	3.66	183.79	27.83	B1	0.01	77
R124	3.66	122.5	-12.10	A1	0.02	619
R600a (Isobutane)	3.63	134.65	-11.87	A3	0	~20
R600 (Butane)	3.80	151.97	-0.55	A3	0	~20
Cyclohexane	4.075	280.49	80.72	A2	0	~20

the minimum value of $(T_{c,k} - T_{cl,k})$ is this way found.

At this level, it's noticed that the limitation at 20 of the total number of segments k is induced [32] by the fact that a higher number needs higher computing time that may be troublesome when an optimization procedure is conducted for the whole working conditions of a considered ORC system.

SIMULATION CONDITIONS

The influence of the fractions of the mixture's base fluids and the temperature glides of different fluid mixtures on the performance of the ORC system, as well as the interaction between the glide and the pinch temperature in the HEXs, are analyzed below with particular simulation conditions. The condenser and the evaporator are assumed to be in counter flow and for both a constraint on the pinch are used in order to avoid unreal HEX size. The pinch constraint value is chosen to be 10 K and 5 K for the evaporator and the condenser respectively. The used ORC conditions are the same as the one's used by former authors [20, 29] and are given in Table 1. The high pressure bubble point temperature is fixed at 90°C and the low pressure dew point temperature is fixed at 35°C. Furthermore, in order to simplify the analysis of the system, the following assumptions have been made:

- All components in each configuration of ORC operate in steady state conditions

Table 3. Comparison between the results of the present study and Ref. [37]

Fluid	C [mole fraction/ mole fraction]	P_e (bar)	$T_{g,evap}$ (°C)	$T_{g,cond}$ (°C)	W_P (kJ/kg)	W_T (kJ/kg)	η_{ORC} (%)	Sources
R245fa/R152a	(1/0)	0.7888	0	0	0.5	25.28	10.403	[37]
R245fa/R152a	(1/0)	0.7890	0	0	0.47	26.20	10.9	Present
R245fa/R152a	(0.9/0.1)	0.9214	7.13	9.58	0.4	21.68	8.682	[37]
R245fa/R152a	(0.9/0.1)	1.0840	6.65	9.53	0.6	22.80	9.2	Present
R245fa/R152a	(0.65/0.35)	1.2960	9.35	12.31	0.7	23.12	8.521	[37]
R245fa/R152a	(0.65/0.35)	1.5870	8.61	12.36	1	24.40	8.95	Present
R245fa/R152a	(0.45/0.55)	1.6250	6.69	9.37	1	26.32	9.128	[37]
R245fa/R152a	(0.45/0.55)	1.8740	6.29	9.47	1.16	27.58	9.6102	Present

- The heat losses to the surrounding environment, and the pressure drops in the connecting tubes are neglected
- The ambient temperature and pressure are 298.15 K and 1 atm, respectively.

Working Fluids

Working fluid selection has wide effects on ORC system. For the chosen ORC configuration without superheating, to avoid two-phase flow in the expander, the used working fluid consists of dry and isentropic mixture [33, 34]. It's established [35] that a dry zeotropic mixture comes from mixing of two pure dry fluids, while a wet zeotropic mixture comes from mixing of two pure wet fluids, and mixing two isentropic pure fluids leads to an isentropic zeotropic mixture. However, mixing two different types of pure fluids could lead to any of the three types, depending on the molar concentration of each fluid.

The seven pure fluids investigated in the present study are listed in Table 2. The related main thermodynamic properties of each tested fluid such as its critical temperature and pressure, the type of its expansion behavior and its environmental, health and safety indices are also shown on the same table.

For the computation conducted in this work, the thermodynamic properties of the used pure or mixture working fluid, were calculated by the Refprop® database from NIST connected with Matlab®.

Validation

The work starts by comparing the present model with the results of Wang et al. [37]. Table 3 shows excellent agreement between the results from [37] and the present study. The relatively small differences are due to the various versions of Refprop® used in the two works.

RESULTS AND DISCUSSION

The Mixture Glide Temperature

In Figures 3, the temperature glides of some used mixture in the present study are illustrated. For a dew temperature of 35°C, the glides of mixtures of Isobutane with R245fa, R141b and with R123 are illustrated with mass fractions of Isobutane varied from 0 to 1. It's noticed that the temperature glide depends significantly on the mass fraction of the base fluids.

Figure 3b shows the temperature glides of the mixtures of butane with R245fa, R141b and with R123. For a dew temperature of 35°C, it's seen that the mixture of butane with R245fa presents an azeotropic behaviour (i.e. a constant temperature, constant pressure phase

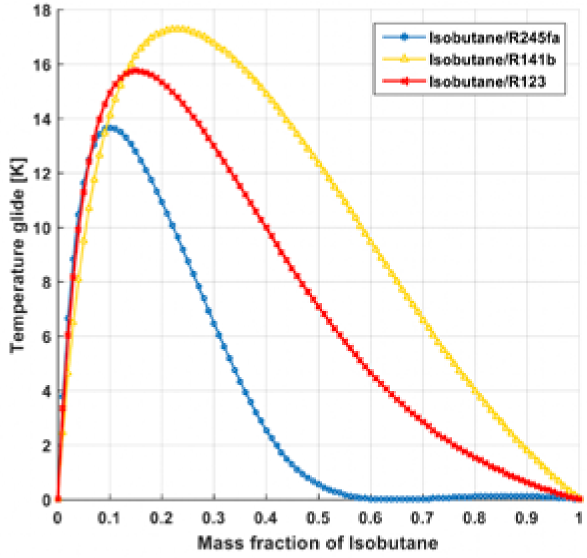

Figure 3.a Temperature glides with a fixed dew temperature of 35 °C for various isobutane fractions in the mixture.

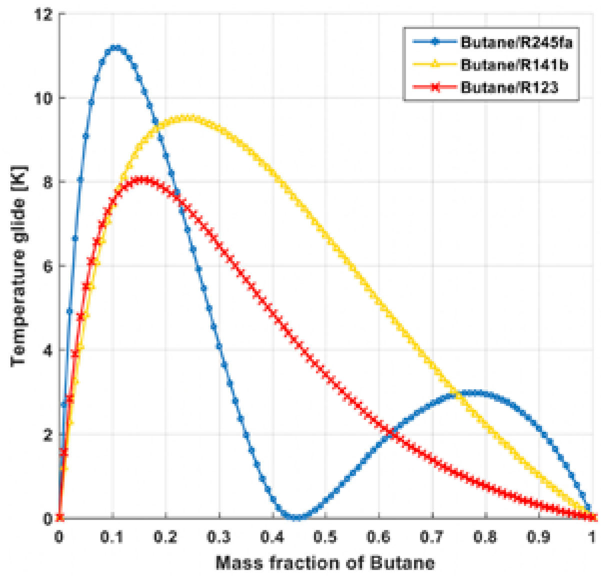

Figure 3.b Temperature glides with a fixed dew temperature of 35 °C for various butane fractions in the mixture.

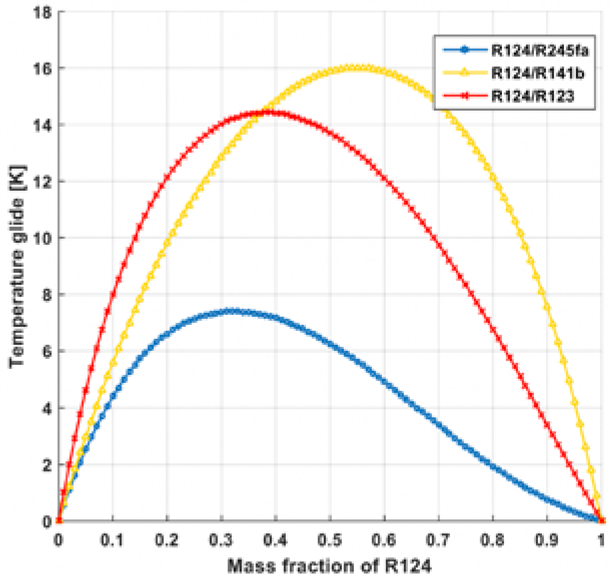

Figure 3.c Temperature glides with a fixed dew temperature of 35 °C for various R124 fractions in the mixture.

change like a pure fluid) for a mass fraction of 0.43 of butane.

The temperature glide that depends on the mass fraction of the mixture of R124 with R245fa, R141b and with R123 for a dew temperature of 35°C in the condenser is shown in Figure 3c. The temperature glide first increases then decreases with the variety of R124 mass fraction. It's seen that due to the largest difference of boiling point, R124/R141b has the largest temperature glides, while the R124/R245fa temperature glides stay lowest.

Evaporator Heat Flow Rate Interaction with the Pinch, Pure Working Fluid Case

The temperature inlet of the working fluid has a significant influence on the heat transfer process in both evaporator and condenser of the ORC system.

In the case of a pure working fluid, giving the inlet heating fluid temperature and mass flow rate (Table 1) and giving the working fluid bubble temperature (Table 1), the evaporator pinch depends on the total heat transfer rate $\dot{Q}_e$ exchanged in the evaporator. In fact $\dot{Q}_e$ is related to the working fluid mass flow rate $\dot{m}_{wf}$ by:

$$\dot{Q}_e = \dot{m}_h \, c_{p,h} \, (T_{h,in} - T_{h,out}) \tag{13}$$

Hence

$$T_{h,out} = T_{h,in} - \frac{\dot{Q}_e}{\dot{m}_h \, c_{p,h}} \tag{14}$$

The evaporator pinch that stands on the working fluid inlet is:

$$pinch = T_{h,out} - T_{bubble,wf} \tag{15}$$

$$T_{pinch} = (T_{h,in} - T_{bubble,wf}) - \frac{\dot{Q}_e}{\dot{m}_h \, c_{p,h}} \tag{16}$$

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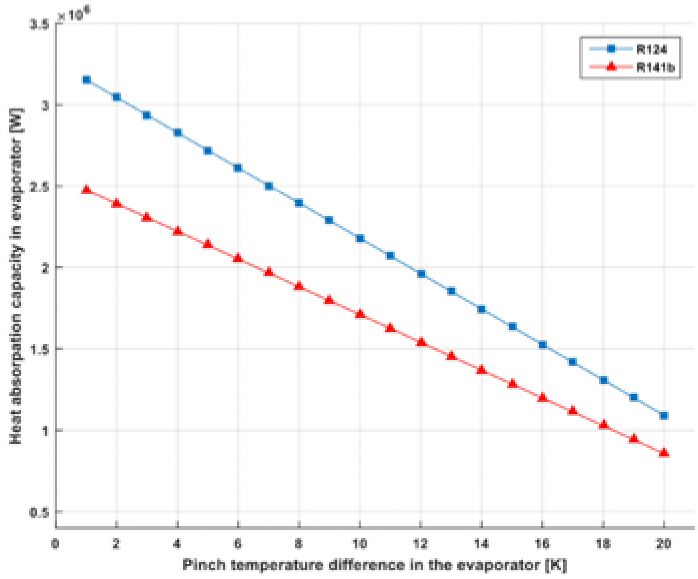

Figure 4 Heat absorption capacity in evaporator for R124 and R141b for various T_{pinch}

If the *pinch* shell remain greater than a pinch limit (*pinch**), knowing $\dot{m}_h$ (Table 1), Eq (16) leads to;

$$\frac{\dot{Q}_e}{\dot{m}_h\, c_{p,h}} < \left(T_{h,in} - T_{bubble,wf}\right) - pinch^* \quad (17)$$

And $\dot{Q}_e < \left(\dot{m}_h\, c_{p,h}\right)\left[\left(T_{h,in} - T_{bubble,wf}\right) - pinch^*\right]$ (18)

It appears that $\dot{Q}_e$ is constrained by the chosen pinch limit *pinch**.

Figure 4 shows the effect of the pinch temperature difference on the heat absorption capacity in the evaporator for R124 and R141b as working fluid for various T_{pinch}. It seen that, whatever is the considered organic fluid, the heat absorption capacity of the heat exchanger decreases with the increase of the pinch temperature difference. It means that the choice of the organic working fluid has a moderate influence on the heat absorption capacity. However, the heat absorption capacity depends significantly on the pinch temperature difference and on the choice of the working fluid.

Evaporator Heat Flow Rate Interaction with the Pinch, Mixture Working Fluid Case

In the case of a mixture working fluid, giving the heat transfer rate $\dot{Q}_e$ in the evaporator, one may compute the pinch value according to Eq (9–10). Figures 5a, b illustrate the temperature profile of the heating fluid and the working fluid for mixture (0.2 cyclohexane / 0.8 R245fa) and (0.4 cyclohexane / 0.6 R245fa) respectively, where the evaporator heat flow rate $\dot{Q}_e$ is 1000 kW.

It seen (Figure 6a) that the pinch for the mixture (0.4 cyclohexane/ 0.6 R245fa) is less than the imposed minimum value *pinch**=10 K. Hence, this mass fraction of (0.4 Cyclohexane/ 0.6 R245fa) is infeasible for a heat rate $\dot{Q}_e$=1000 kW. It may concluded that giving a mixture, giving a pinch constraint (*pinch**), and a desired heat transfer rate on the evaporator $\dot{Q}_e$ there exist mass fractions that are not consistent with those operating conditions. This leads to an infeasible mass fraction zone for each operating condition. This

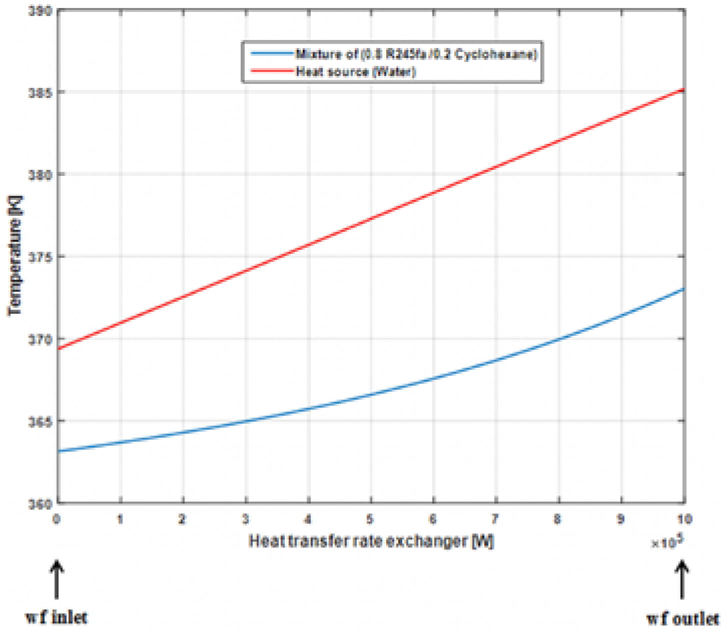

Figure 5.a 0.8 R245fa/ 0.2 Cyclohexane mixture.
Fluids temperature profile in the Evaporator.

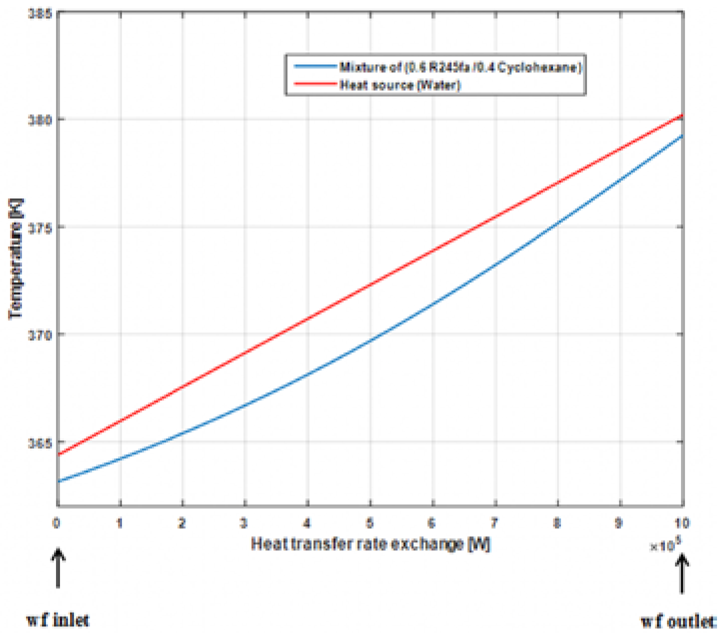

Figure 5.b 0.6 R245fa/ 0.4 Cyclohexane mixture.
Fluids temperature profile in the Evaporator.

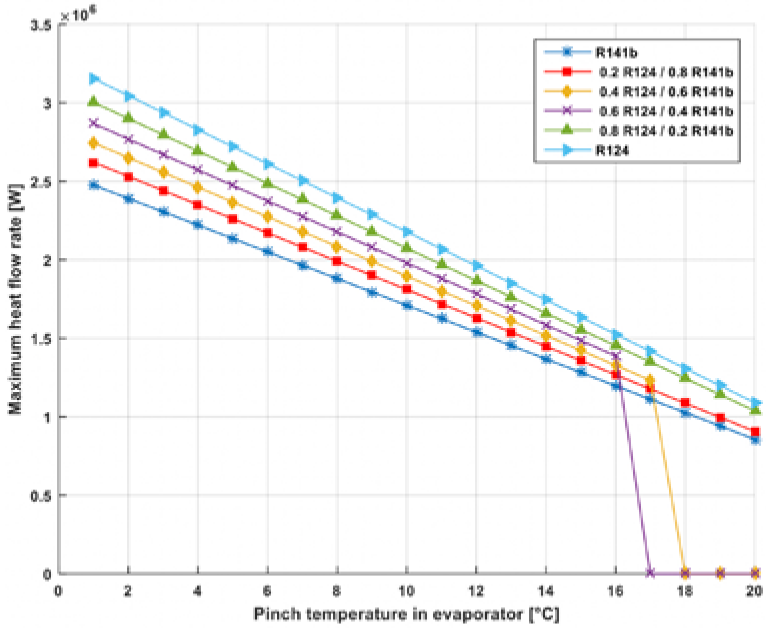

Figure 6.a Maximum heat flow rate capacity in evaporator for various pinch

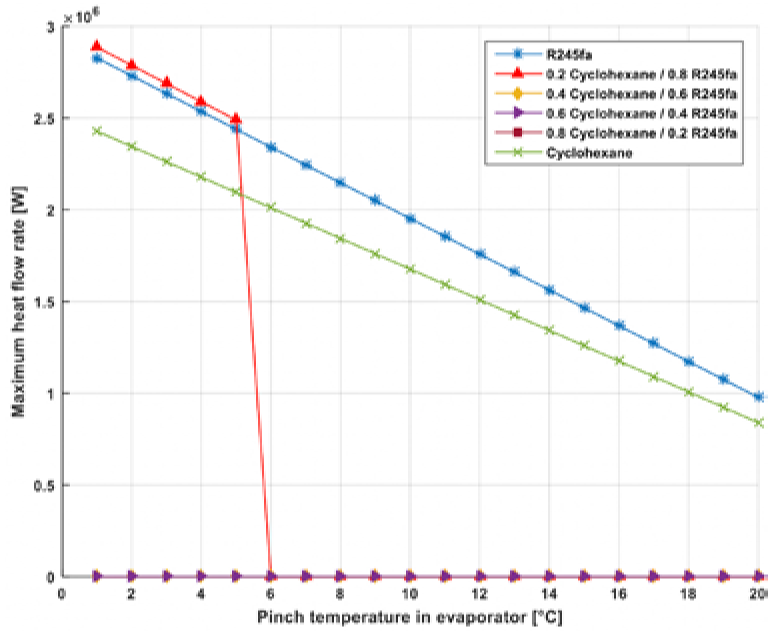

Figure 6.b Maximum heat flow rate capacity in evaporator for various pinch

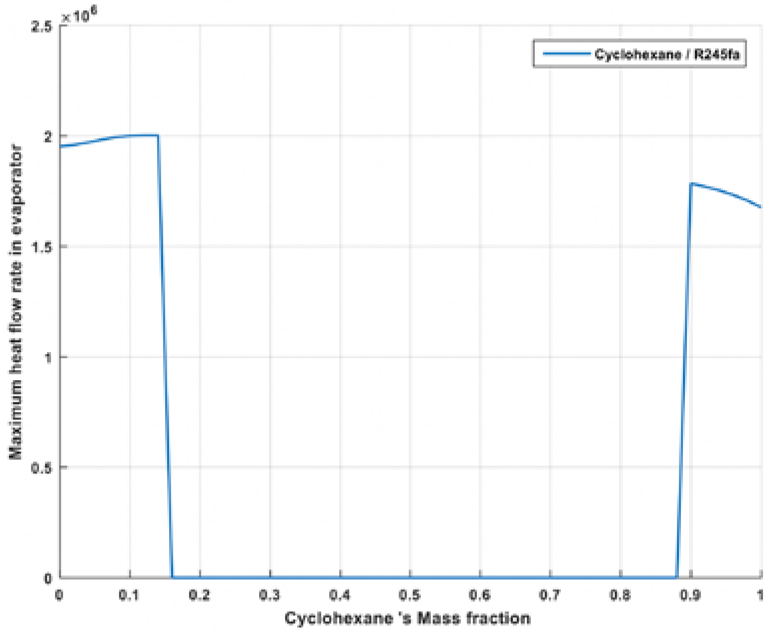

Figure 7. a infeasible zone for (cyclohexane/ R245fa), with pinch limit 10K in the evaporator

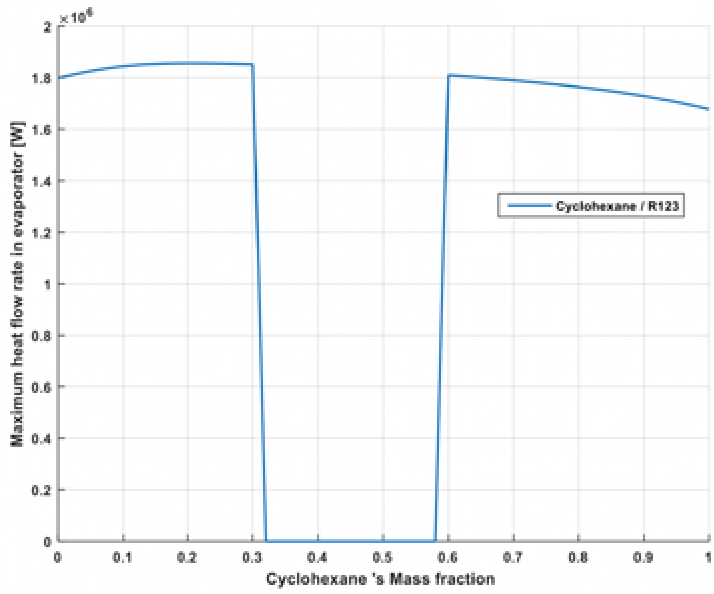

Figure 7.b infeasible zone for (cyclohexane/ R123), with pinch limit 10K in the evaporator

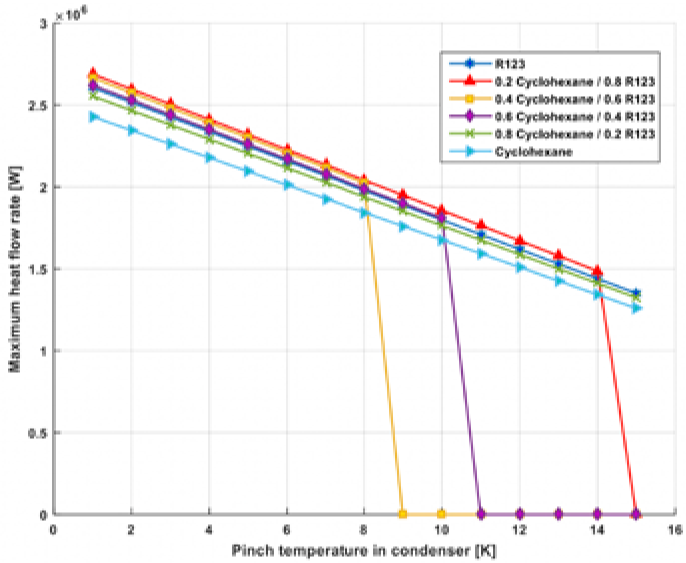

Figure 8.a Maximum heat flow rate capacity in condenser for various pinch

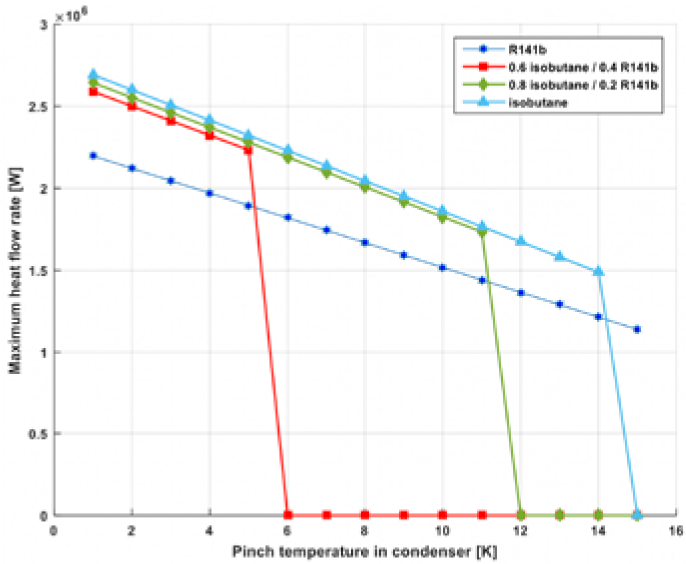

Figure 8.b Maximum heat flow rate capacity in condenser for various pinch

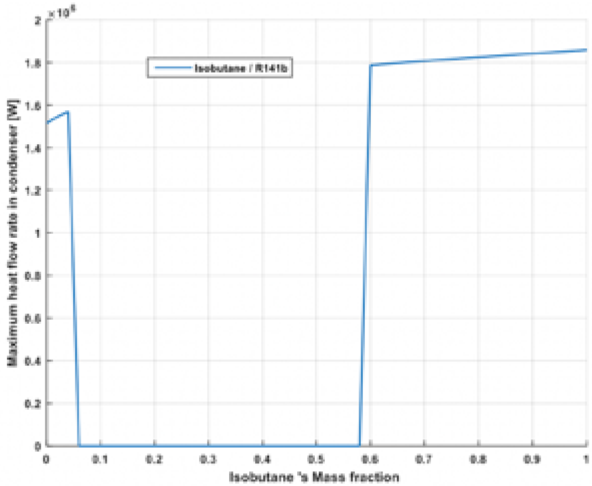

Figure 9. a global infeasible zone for (isobutane/ R141b), with pinch limit 5 K in the condenser

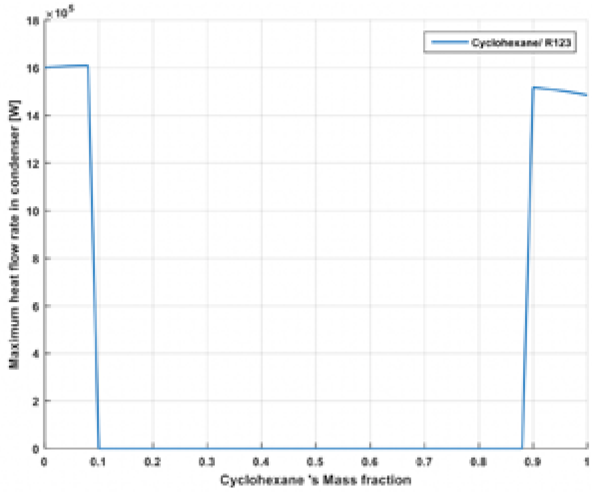

Figure 9. b global infeasible zone for (cyclohexane/ R123), with pinch limit 5 K in the condenser

is the consequence of the interaction between the imposed minimum pinch and the mixture glide.

Giving the operating condition (Table 1) for heating fluid mass flow rate ($\dot{m}_h$), its inlet temperature ($T_{h,in}$), and the working fluid bubble temperature ($T_{bubble,wf}$), the pinch limit ($pinch^*$) interact with the used mixture temperature glide and hence there will be a maximum evaporator heat flow rate ($\dot{Q}_e$).

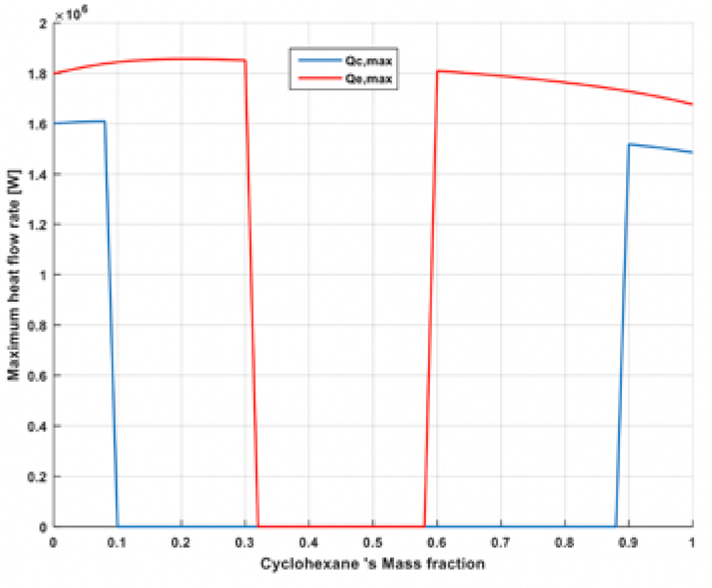

Figure 10 global infeasible zone for (Cyclohexane/ R123), with pinch limit 10 K and 5 K in the evaporator and the condenser respectively

Figure 6a illustrate for a various mixture, the maximum $\dot{Q}_{e,\max}$ that the working fluid may exchange in the evaporator. $\dot{Q}_{e,\max}$ is obviously related to the correspondent working fluid flow rate $\dot{m}_{wf,max}$ by $\dot{Q}_{e,\max}$=$\dot{m}_{wf,max}\,(h_3 - h_2)$.

Figure 6b illustrate for the special case of (0.4 cyclohexane/ 0.6 R245fa). It appears that there are *pinch** value that leads to null maximum evaporator heat flow rate $\dot{Q}_{e,\max}$. Temperature glide value is particularly. It is noticed from Figure 3c that (0.4 R124 / 0.6 R141b) mixture presents greater glide than mixture (0.2 R124 / 0.8 R141b). It seen then the greater is the glide the small is the limit pinch (*pinch**) that leads to non-null $\dot{Q}_{e,\max}$.

Figures 7a, b show for giving *pinch**=10 K that for the considered mixture (Cyclohexane/ R245fa), there exist mass fraction intervals (we call then the 'infeasible zone') that leads to null $\dot{Q}_{e,\max}$.

The Pinch-Glide Interaction in the Condenser

In the condenser, the cooling fluid inlet temperature $T_{cl,in}$ is generally set given [23], as well as the working fluid dew point $T_{dew,wf}$. With this giving condition the same above HEX exposed behavior and interaction between the glide and the pinch limit may occur if the cooling fluid mass flow rate is set given. Hence, for a giving pinch limit *pinch** in the condenser, for each mixture one may experience null $\dot{Q}_{c,max}$.

Figure 8a illustrate for a various mixture, the maximum $\dot{Q}_{c,max}$ that the working fluid may exchange in the condenser. $\dot{Q}_{c,max}$ is obviously

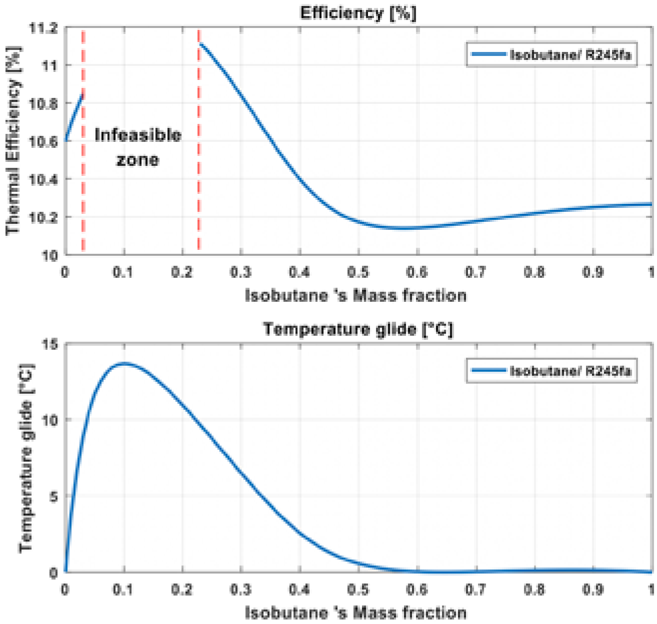

Figure 11.a Thermal efficiency and temperature glides for various isobutane mixing fractions with R245fa.

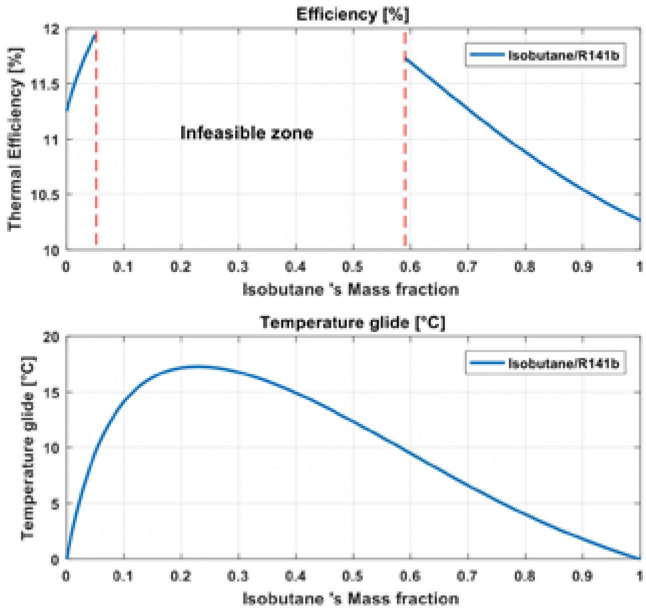

Figure 11.b Thermal efficiency and temperature glides for various isobutane mixing fractions with R141b.

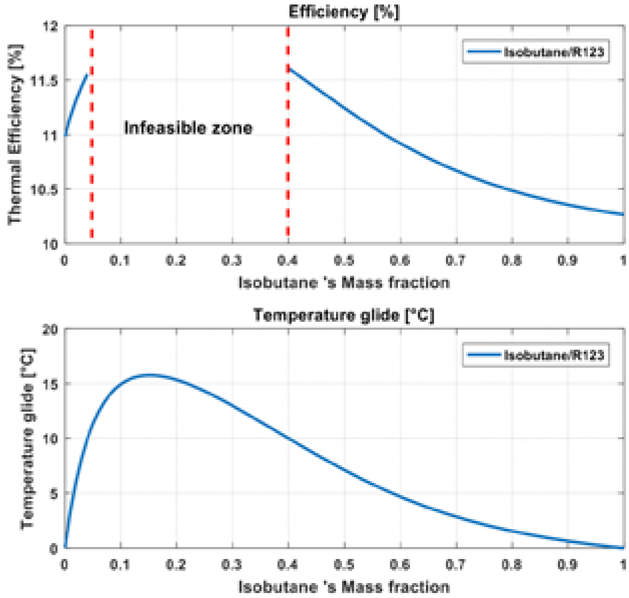

Figure 11.c Thermal efficiency and temperature glides for various isobutane mixing fractions with R123.

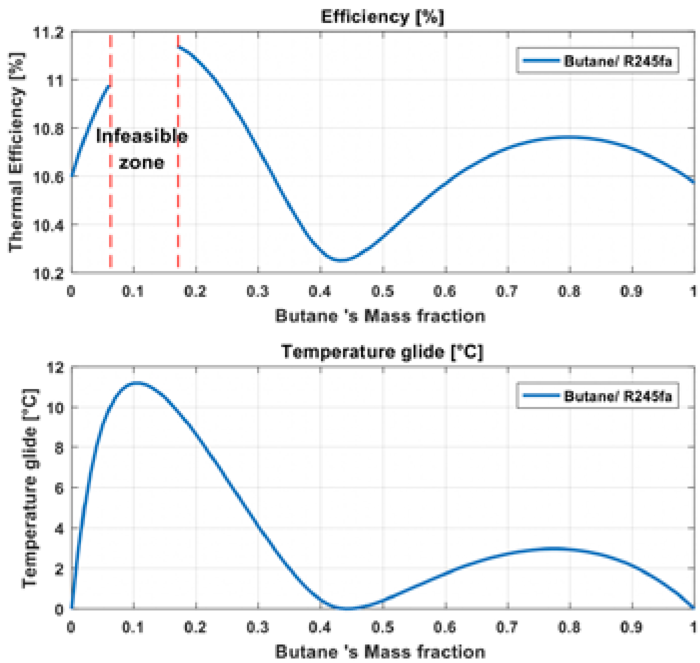

Figure 12.a Thermal efficiency and temperature glides for various Butane mixing fractions with R245fa

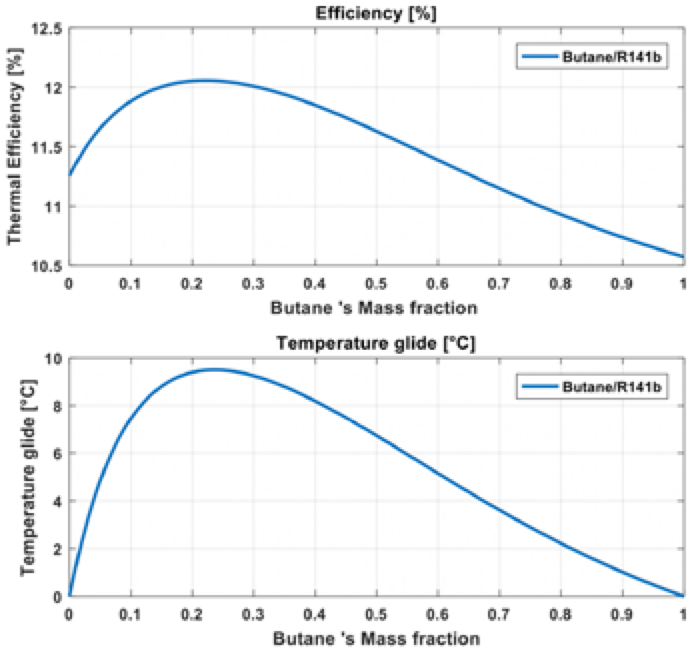

Figure 12.b Thermal efficiency and temperature glides for various Butane mixing fractions with R141b

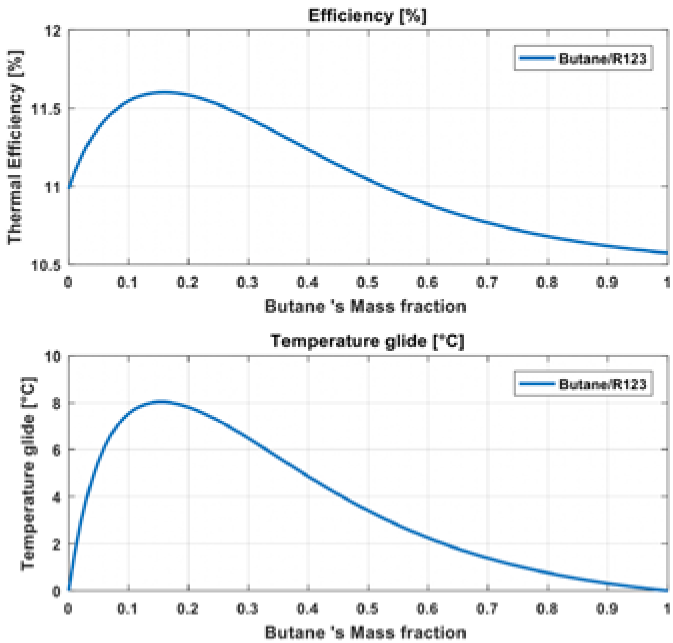

Figure 12.c Thermal efficiency and temperature glides for various Butane mixing fractions with R123

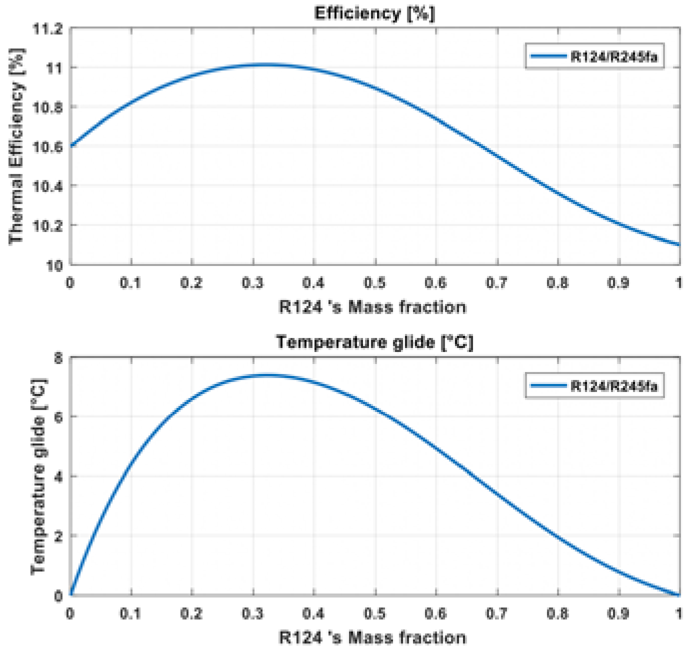

Figure 13.a Thermal efficiency and temperature glides for various R124 mixing fractions with R245fa

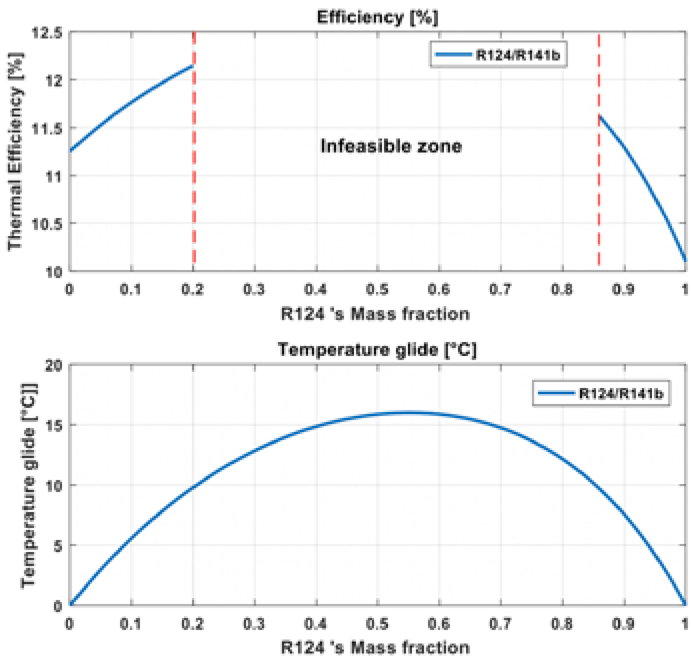

Figure 13.b Thermal efficiency and temperature glides for various R124 mixing fractions with R141b

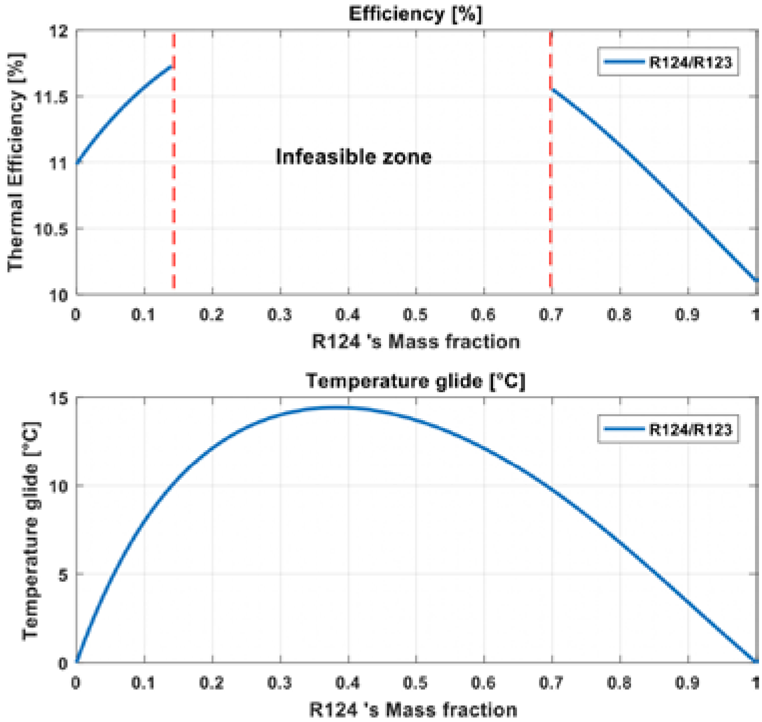

Figure 13.c Thermal efficiency and temperature glides for various R124 mixing fractions with R123

related to the correspondent working fluid flow rate $\dot{m}_{wf,max}$ by $\dot{Q}_{c,max}=\dot{m}_{wf,max}\,(h_4 - h_1)$.

Figure 8b illustrate for the special case of (0.2 isobutane/ 0.8 R141b). It appears that there are *pinch** value that leads to null maximum evaporator heat flow rate $\dot{Q}_{e,\mathrm{max}}$. Temperature glide value is particularly. It noticed from Figure 3a that (0.2 isobutane/ 0.8 R141b) mixture presents greater glide than mixture (0.6 isobutane/ 0.4 R141b). It seen then the greater is the glide the small is the limit pinch (*pinch**) that leads to non-null $\dot{Q}_{c,max}$.

Finally, mass fraction infeasible zone for each mixture, may be due to the glide-pinch interaction in the evaporator and/ or in the condenser.

Figure 9a, b illustrate the global infeasible zone for (Cyclohexane/ R123) and (Isobutane/ R141b) respectively.

Figure 10 illustrate the global infeasible zone for (Cyclohexane/ R123); with pinch limit 10 K and 5 K in the evaporator and condenser respectively.

The pinch limits were 10 K and 5 K in the evaporator and condenser respectively. Notice that the infeasible zone in the condenser may be escaped by varying the cooling fluid mass flow rate.

Finally, notice that the infeasible zone in the condenser may be escaped by varying the cooling fluid mass flow rate.

Thermal Efficiency of ORC System Using Mixture

The comparison of the results of the thermodynamic analysis are presented in this section. The mass fraction effects of different zeotropic mixtures on the system thermal efficiency are shown in figures. Taken into account that for a specified working condition and pinch limits, there may exist infeasible mass fraction zone, thermal efficiency for the chosen single ORC system (Fig. 1a) is studied. The working conditions are those specified on Table 1, and the pinch limits are $pinch_e^* = 10$ K and $pinch_c^* = 5$ K in the evaporator and condenser respectively. To illustrate the sole effect of the pinch-glide interaction in the evaporator, the cooling fluid flow rate is not specified. It has been varied in such way that the condenser pinch remains higher than the specified $pinch_c^*$.

Figures 11 show the variation of the thermal efficiency with the isobutane mass fractions. The thermal efficiency increases first, and then decreases with the increase of the temperature glide of the mixtures. Thus, the use of zeotropic mixture can decrease the temperature difference between the heat source and the working fluid, which will reduce the heat transfer irreversibility and increase the cycle efficiency.

This is observed for other mixtures as shown in Figure 12 and Figure 13. Higher temperature glide leads to lower temperature differences between the working fluid and heat source, and hence decreases the irreversible loss during the heat transfer.

Comparing the pure working fluids, the ones with high critical temperature have shows higher thermal efficiency than the one with lower critical temperature. For the working fluid with high critical temperature, the maximum thermal efficiency of R141b can reach up to 11.6%. While for the working fluids with low critical temperature, the maximum thermal efficiency of R124 is 10 %. This is because the evaporation temperature of high critical temperature working fluid is higher than low critical temperature working fluid and leads to relatively lower irreversibilities.

For the mixture with no infeasible zone, Figure 12b, c and Figure 13a it shows that the maximum efficiency corresponds the maximum glide in the evaporator.

Figures 11–13 show for different mixture the correspondent's infeasible zones and glide value. Notice that whenever the mixture glide is at the same level of the pinch limit, it leads to infeasible zones. For the mixtures R245fa/ butane and R245fa/ isobutane that present an azeotropic fraction shown in Figures 11a, Figure 12a, the ORC efficiency with this mixture is the lesser with the azeotropic fraction.

Figures 14 illustrate the mass fraction effects on the thermal efficiencies for mixture with high temperature glide up to 18°C. They show large infeasible mass fraction zones because of the higher interaction between the mixture glide temperature that induces fluids temperature difference lower than that imposed constraint on the pinchs' values in the evaporator and in the condenser. For Figures 11–14, it concluded that ORC thermal efficiency is systematically higher with a mixture that with the corresponding pure fluids.

From Figures 11–14, it may conclude that if a mixture of two pure fluids don't present an azeotropic fraction, the efficiency using the mixture is always higher whatever is the mass fraction than the pure fluid that shows

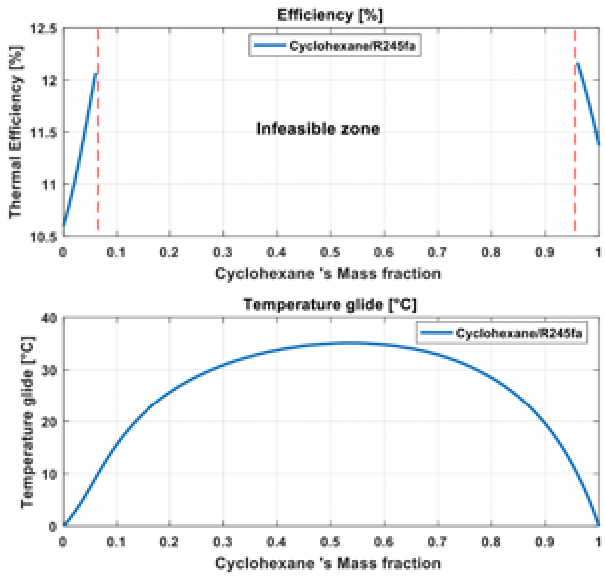

Figure 14.a Thermal efficiency and temperature glides for various Cyclohexane mixing fractions with R245fa

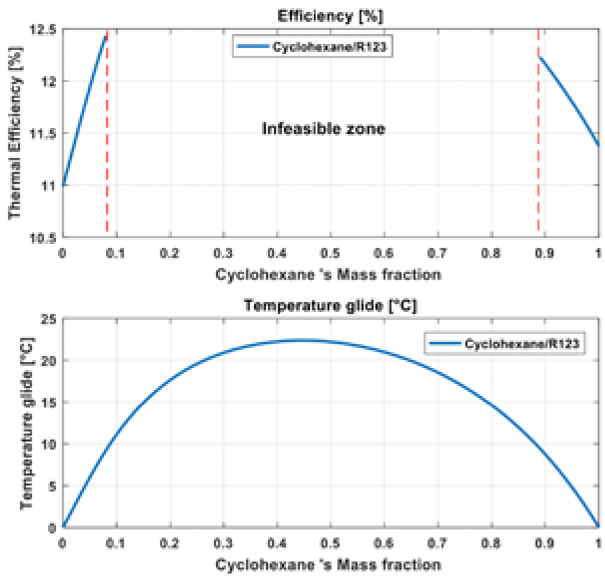

Figure 14.b Thermal efficiency and temperature glides for various Cyclohexane mixing fractions with R123

the lesser efficiency. As an example in Figure 11b, the ORC using mixture isobutane/R141b presents efficiency always higher than the efficiency of ORC using isobutane.

CONCLUSION

It's pointed out in this study that some pure fluid mixture, shows "unfeasible fluid's fraction zone" that leads to temperature difference of the fluids in the HEXs that are below than the desired pinch values.

Furthermore, seven refrigerants and their binary mixtures were evaluated as working fluid for Organic Rankine Cycle (ORC) system with emphasis placed on the interaction between temperatures glides and heat exchangers pinchs in both evaporator and condenser. The parameters of the ORC systems are performed with constraint on the pinchs values for both evaporator and condenser, and performance of the ORC system using these different mixture working fluids are compared and analyzed using the same parameters. The main conclusions based on the studded pure fluids and mixtures can be summarized as follows:

- The constraint on the pinchs (i.e the fluid's temperature difference in the HEXs) avoids the rise of situation with unreal HEXs dimension and have to be considered and checked thorough the HEXs in all simulation/optimization ORC systems that involves mixtures with temperature glides.
- For all the seven studded fluid mixture, there exist mass fraction range(s) that is (are) not consistent with the pinch values in the HEXs: so called "infeasible zone" appears because of to the interaction between the mixture glide temperature and the constraint on the pinchs value in the evaporator and in the condenser.
- For the fluids' mixtures without infeasible zone, the maximum thermal efficiency corresponds to fluids' fraction mixture with the maximum glide.
- When the mixture has an azeotropic point, the lowest thermal efficiency corresponds to a working mixture fluid with the azeotropic fractions.
- For each mixture, which hasn't an azeotropic point, the thermal efficiency of the ORC systems is better than the corresponding pure fluids.

NOMECLATURE

Symbols

c_p	Constant pressure specific heat [kJ kg^{-1} K^{-1}]
P	Pressure [kPa]
T	Temperature [K]
$\dot{Q}$	Heat absorption capacity [kW]
$\dot{W}$	Power output [kW]
$\dot{m}$	Mass flow rate [kg s^{-1}]
h	Specific enthalpy [kJ kg^{-1}]
x	Mole fraction [-]
ΔT	Temperature difference

Acronyms

HEX	Heat exchanger
ORC	Organic rankine cycle
Yrs	Year

Greek symbols

η	Cycle efficiency [%]

Subscripts and superscripts

B	Boiling point
Cr	Critical point
C	Condenser
cl	Heat sink
e	Evaporator

GWP	Global warming potential
G	Glide
in	Inlet
h	Heat source
T	Turbine
ODP	Ozone depletion potential
out	Outlet
P	Pump
wf	Working fluid
*pinch**	Pinch limit
max	Maximum
min	Minimum
net	Net power output

AUTHORSHIP CONTRIBUTIONS

Authors equally contributed to this work.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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