Working fluid selection general method and sensitivity analysis of an Organic Rankine Cycle (ORC): application to Ocean Thermal Energy Conversion (OTEC)

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Highlights

- Development of a general model for the choice of the working fluid using Entropic Mean Temperature Difference.
- Comparison of 26 working fluids over 107 according to four criteria: technicity of the installation, security, environmental impacts and thermodynamic performances.
- Good candidates for an application to OTEC: NH_3, R507a and R1234yf
- Parametric sensitivity analysis of the model.

Keywords

Ocean Thermal Energy Conversion (OTEC); Entropic Mean Temperature Difference (EMTD); Organic Rankine cycle (ORC); parametric sensitivity analysis.

Abstract

A general model of an ORC (Organic Rankine Cycle) that is applicable to various technologies of heat exchangers has been carried out. It has been done considering the entropic mean temperature difference between the heat source and the working fluid as a parameter for heat exchangers. This model allows to compare pure fluids and mixtures in similar operating conditions. Simulations were conducted in the case of OTEC (Ocean Thermal Energy Conversion), for which the inputs are based on experimental measurements on an onshore prototype in Reunion Island. 26 fluids have been compared, considering thermodynamic performances (thermal efficiency and volumic work), technicity, security and environmental impacts. In the end, NH_3, R507a and R1234yf appears to be the most suitable ones. In order to have a better understanding of the model and to determine its validity in the whole domain of variation of the parameters for OTEC, a parametric sensitivity analysis has been carried out by ANOVA (ANalysis Of VAriance) associated to polynomial chaos expansion method. The most sensible parameters are heat source temperature, heat exchangers entropic mean temperature difference and turbine isentropic efficiency. The ranking given for the fluids is still valid in the whole range of the parameters for OTEC.

1. Introduction

Ocean Thermal Energy Conversion (OTEC) is a great opportunity in the tropical belt to produce non-fluctuant and environmentally friendly power [1]. The temperature difference between hot surface and cold deep seawater is exploited through a power cycle in order to produce electricity [2]. The temperature difference between hot and cold heat sources is very small compared to conventional Rankine cycles, or even compared with other applications working at low temperature, such as solar, geothermal or waste heat recovery [3].

Various approaches are used in order to increase the very low performance of an ORC (Organic Rankine Cycle):

- modifying the cycle structure,
- optimizing the working conditions of the cycle,
- choosing the most adapted working fluid for the application.

Considering the first point, Tchanche *et al.* have reviewed a lot of modified cycles (with a reheater for instance), or mixtures-adapted cycle like the Kalina cycle or Uehara cycle [4]. In parallel, Yoon *et al.* proposed an ammonia-based power cycle by using an expansion valve and a cooler [5] and Yuan *et al.* presented a water-ammonia based power absorption cycle with two ejectors [6]. They both obtained better thermal efficiency than the conventional ORC, even if the Kalina and Uehara cycles also show good performances [7]–[11]. Nonetheless, the basic ORC appears to be the simplest, and provides reliability, low investment costs, and easy maintenance [12].

Considering the choice of the working fluid, various criteria and methods have been proposed to select the most suitable fluids. The main ones for a working fluid are good thermodynamic performances, non-toxicity, small environmental impact, low cost, availability, and compatibility with pipes and components materials. Unfortunately, it is difficult to find the perfect fluid that meets all of these qualities. Lee *et al.* [13] compared the performances of more than one hundred ozone-safe working fluids for an ORC applied to waste heat recovery. They found that thermodynamic performances of the fluids are correlated with their physical properties, such as normal boiling point, critical pressure and molecular weight. Stijepovic *et al.* [14] also carried out a theoretical study to evaluate the effect of physical properties of workings fluids on thermal and exergetic efficiency and the ratio of heat exchangers area and net power output. Saleh *et al.* [15] conducted simulations to compare the thermal efficiency and volume flow rates of various working fluids for different types of cycle. Wang *et al.* [16] provided a theoretical analysis of net power output and heat exchangers surface for a Waste Heat Recovery (WHR) system. They found that fluids with low Jacob number performed better. They also found in another study [17] that the choice of the working fluid for WHR has a small impact on optimal performances of the cycle, and that the evaporator is the most important component in exergy losses. However, they only consider pure fluids. The use of mixtures as working fluid has also been discussed [18], [19]. It is established that, in theory, the behavior of mixtures during phase change allows reducing the mean temperature difference between working fluid and source in heat exchangers, but the performance is not always better than pure fluids in practice. Some authors realized a complete cost study by using correlations for several components [17], [20]–[22]. This means that they should choose a precise technology of heat exchangers and expander. Zhang *et al.* [23] proposed a method using the Hass Diagram Technique to compare working fluids with thermodynamic, security and environment considerations. However, no simulation was conducted to evaluate thermodynamic behavior of each fluid in a particular cycle.

The selection of the best fluids is also often related with the optimization of working conditions parameters of the cycle, like the evaporation and condensation temperature : each fluid is thus compared with his own optimized parameter [16], [24], [25]. He *et al.* [26] carried out an analytical study in order to evaluate the optimized evaporation temperature with net power output as the objective function and compared the optimal net power output for several fluids. In that case, the objective function is decisive, as it influences the value of optimal parameters. Therefore, some efforts have been made to conduct multi-objective optimization [27], [28].

Moreover, in the case of OTEC, which is very particular due to the weak temperature difference between heat sources, the literature about the choice of the working fluid is relatively poor. Sun *et al.* [29] provided an analytical method to optimize the performance of an OTEC power plant considering two working fluids, R134a and ammonia. Yang *et al.* [30] conducted an optimization of evaporation and condensation temperature and a comparison of five pure working fluids considering an OTEC power plant with shell-and-tube heat exchangers. Yoon *et al.* [31] compared the influence of various working fluids on the thermal efficiency of an OTEC power plant, but they didn't take into account net power output or volume flow rates. Iqbal *et al.* [32] analyzed the influence of mixtures on the performances of an OTEC system, but they compared only one of them with one pure fluid (propane). Hung *et al.* [33] carried out a comparison of eleven working fluids for solar and OTEC heat sources based on a study of physical properties of the fluids. They found that isentropic fluids performed generally better. Furthermore, some attention has been paid on increasing the temperature difference between the cold and the hot sources of an OTEC system by coupling it with solar energy [34], [35] or with the effluent of a nuclear power plant [36]. The problem is that the power produced is no longer steady during all day and night, and nuclear power plant are often not available in tropical islands, where OTEC seems undoubtedly to be a good opportunity. In fact, little attention has been paid on comparing both pure and mixed working fluids for OTEC.

The previous short review shows that a lot of studies have been carried out for optimizing the performances of an ORC, from simple approaches using ideal cycles (preselecting the fluid before designing and sizing the components), to detailed energetic and economic studies and simulations (where design and size of the components are fixed). These last methods require a good knowledge about the technology of the system and its components, and are therefore not applicable in a preliminary design phase of the system. As the choice of the working fluid occurs early in the conception of an ORC, simple approaches are generally preferred. In this case, the comparison of very different fluids (in particular when comparing pure fluids and mixtures) remains tricky, especially when heat exchangers are not particularly described. To do so, some authors introduce the pinch point [17], [25], defined by the minimal temperature difference between the working fluid and the heat transfer fluid in the HEX (Heat Exchanger). However, the location and the value of the pinch point depend on the fluid, the flow rates and the amount of heat exchanged and are sometimes difficult to determine and require a deep knowledge of the HEX structure and applied conditions. Other authors consider the temperature difference between the outlet of the working fluid and the inlet of the heat source [5], [6], [37]. This method is interesting when comparing pure fluids, because the phase change temperature is constant. In the case of zeotropic mixtures, temperature is no longer constant during evaporation and condensation and this behavior allows to reduce the mean temperature difference between the working fluid and the heat source [18]. However, the temperature variation of the mixture does not necessarily have the same profile as the heat source. Hence, one or more pinch points can be observed [38]. So, when comparing zeotropic mixtures with pure fluids, this method becomes disadvantageous.

To overcome these drawbacks and provide a general method to compare working fluids in similar conditions with a reduce number of hypothesis, the entropic mean temperature difference is introduced in this study as a parameter for heat exchangers description. In the end, a general method for working fluid comparison is given, considering four criteria: technicity, thermodynamic performances, security and environment. This method is implemented for an OTEC application, for which input parameters are issued from an experimental land-based prototype in Reunion Island [39]. A parametric sensitivity analysis of the model is then carried out in order to explain the model operation, and to give the validity domain of previous results.

2. Cycle description

2.1. From the ideal Carnot cycle to the real ORC

The most efficient cycle for converting heat into work is the Carnot cycle (Figure 2.a). However, this ideal cycle is not found in practice and is replaced by the Rankine cycle (Figure 2.b). The latter is composed of four components: a pump (P), an evaporator (E), a turbine (T) and a condenser (C), as shown in Figure 1. A working fluid in the liquid state (point 1) is evaporated by using the heat from the hot source. The obtained vapour at high pressure (point 2) is expanded in the turbine producing mechanical work convertible in electricity. The vapour at low pressure (point 3) is then cooled and condensed by using the cold source (point 4). A pump brings back this liquid to the inlet of the evaporator (point 1). In the case of so called "wet fluids" (i.e. fluids with a negative slope of their vapour saturation curve $(\partial T/\partial s)_{x=1} < 0$), the fluid leaves the turbine in a two-phase flow, leading to droplets (Figure 2.c), whereas in the case of so called "dry" or "isentropic" fluids (i.e. fluids with a positive slope or with a vertical vapour saturation curve, respectively), the fluid at the output of the turbine is overheated (Figure 2.d and 2.e).

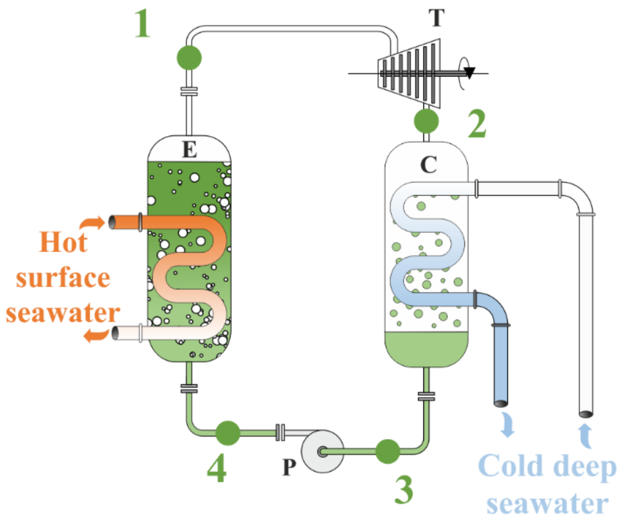


Figure 1. Schematic of a basic ORC applied to OTEC (E: Evaporator, T: Turbine, C: Condenser, P: Pump)

Furthermore, an ORC undergoes various unideal behaviors:

- Due to heat exchangers, a temperature difference appears in the cycle between the working fluid and heat sources. Moreover, a little overheat or subcooling is often observed at the outlet (Figure 2.c, 2.d and 2.e).
- The pump and the turbine are not perfect: the transformations occurring are in reality producing entropy, so the isentropic efficiency of these components has been considered.
- In the particular case of low grade heat ORC, heat exchangers areas are very important, so as the pressure losses can be important, particularly for plate heat exchangers.

For an ORC applied to OTEC, the temperature difference between hot surface seawater (T_{hw} = 25.5 °C) and cold deep seawater (T_{cw} = 5 °C) is very small, and the corresponding ideal thermal efficiency of the Carnot cycle (given by: $h_{th} = 1 - T_{cw} / T_{hw}$) is only 6.9 %.

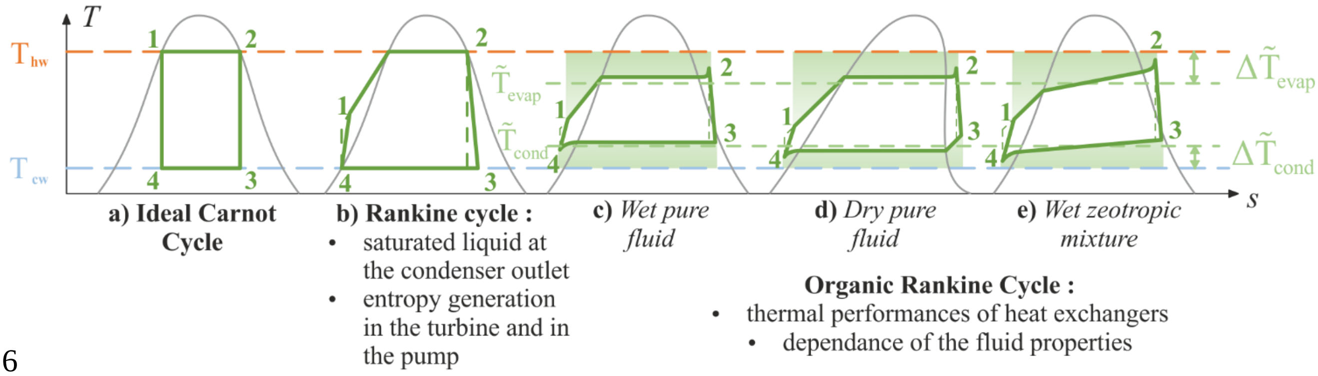


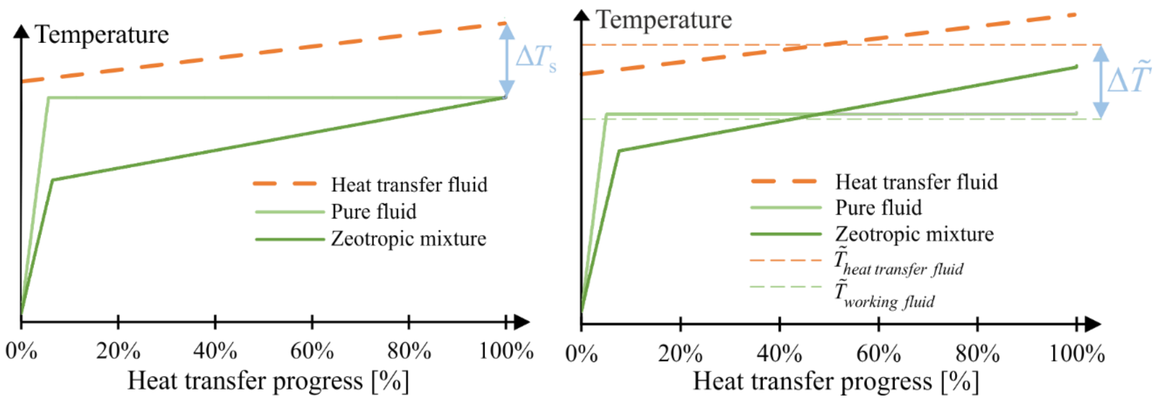
Figure 2. T-s diagram of thermodynamic cycles progressing from ideal to real

2.2. Cycle modeling

To avoid the drawbacks of the Pinch Point approach, it has been decided to introduce the Entropic Mean Temperature Difference (EMTD) concept. The latter is, by definition, the ratio of the enthalpy change to the entropy change, that is to say, the harmonic mean of temperature weighted by heat transfer, and is given by:

$$\tilde{T} = \frac{\int \delta q}{\int \delta q / T} = \frac{q}{\Delta s} = \frac{\Delta h}{\Delta s} \tag{1}$$

This notion was used by Meunier *et al.* [40] for thermodynamic cycle analysis and by other authors [41]–[43]. The EMTD is then defined by the difference between entropic mean temperatures of both working and heat transfer fluids. This parameter is advantageous comparing to the most used temperature difference at the output ΔT_s since it allows the comparison between pure fluids and mixtures. For the mixture, the mean temperature difference is greater than that of the pure fluid due to the temperature glide. When using EMTD, fluids can be compared in more similar operating conditions in terms of heat transfer, as shown in Figure 3.



3.a. Case when ΔT_s is fixed *3.b. Case when $\Delta\tilde{T}$ is fixed*

Figure 3. Typical temperature evolution profile in an evaporator throughout the heat transfer progress for a pure fluid and a mixture.

So as to compare different kind of working fluids, it can be supposed that the entropic mean temperature of the heat transfer fluid is the same for all the working fluids, taken equal to the input source temperature. EMTD in the evaporator and in the condenser are then given by:

$$\Delta\tilde{T}_{evap} = T_{hw} - \tilde{T}_{evap} \tag{2}$$

$$\Delta\tilde{T}_{cond} = \tilde{T}_{cond} - T_{cw} \tag{3}$$

Furthermore, considering the pump and the turbine, they are described by their respective isentropic efficiency:

$$\eta_{pump} = (h_1^{is} - h_4) / (h_1 - h_4) \tag{4}$$

$$\eta_{turb} = (h_3 - h_2) / (h_3^{is} - h_2) \tag{5}$$

Energy balances for each component are given by:

Evaporator: $$q_{evap} = h_2 - h_1 \tag{6}$$

Turbine: $$w_{turb} = h_2 - h_1 \tag{7}$$

Condenser: $$q_{cond} = h_4 - h_3 \tag{8}$$

Pump: $$w_{pump} = h_1 - h_4 \tag{9}$$

The performance of the cycle is then determined by two parameters: the widely used thermal efficiency and the net volumic work respectively determined by:

$$\eta_{th} = w_{net} / q_{evap} = (w_{turb} + w_{pump}) / q_{evap} \quad (10)$$

$$w_{net,\,vol} = w_{net} / v_3 = (w_{turb} + w_{pump}) / v_3 \quad (11)$$

Where v_3 is the maximum value of the specific volume of the working fluid at the turbine output. In fact, as the work consumed by the pump is small compared to the work produced by the turbine, this parameter is approximately the inverse of the Size Parameter (SP) used by He *et al.* [26], Macchi *et al.* [44], Lakew *et al.* [45] and Baik *et al.* [46] and allows having an idea of the turbine size.

3. Working fluid selection

A method for the comparison of working fluids based on the use of the precedent model has been developed and applied to OTEC. Fluids are compared according to 4 criteria: technicity, security, environmental impacts and thermodynamic performances. Methods and results are shown in this section.

3.1. Simulation hypothesis

The system is considered to be working under steady state conditions and heat losses are neglected. The properties of both pure working fluids and mixtures have been determined using the software Engineering Equation Solver (EES) [47]. Input parameters have been obtained from an OTEC onshore prototype situated in Reunion Island [48], [39] (an overseas French department located in Indian Ocean, close to Mauritius). Corresponding values are listed in Table 1.

Table 1 : Input parameters used for simulations

External conditions	
Hot seawater temperature (T_{hw})	25.5°C
Cold seawater temperature (T_{cw})	5°C
Evaporator	
Overheating (ΔT_{over})	0.1°C
Pressure losses (ΔP_{evap})	0.15 bar
EMTD ($\Delta\tilde{T}_{evap}$)	4°C
Condenser	
Subcooling (ΔT_{sub})	0.1°C
Pressure losses (ΔP_{cond})	0.15 bar
EMTD ($\Delta\tilde{T}_{cond}$)	4°C
Pump and turbine characteristics	
Pump isentropic efficiency (η_{pump})	0.8
Turbine isentropic efficiency (η_{turb})	0.8

Otherwise, for an OTEC application, the low temperature difference between hot and cold heat sources involves very important heat exchange areas and volumes. So, pressure drop can be observed in the working fluid side, particularly for plate HEX and have been assumed to occur during the phase change of the fluid.

The results obtained for a list of selected working fluids is shown in Table 3.

3.2. Technicity

The first criterion used to compare working fluids in this study is the technicity represented by the working pressure range and the vapour quality at the turbine outlet. Extreme pressures of the cycle are calculated considering sources temperatures, while nominal pressures are determined by simulated working fluid temperatures. A pressure that ranges between 1 and 24 bar has been considered here and provides generally easier implementation and lower cost. Furthermore, the vapour quality is chosen greater than 97 % to reduce the risk of alteration of the turbine by any droplets. After a first selection between a list of 107 fluids according to these criteria, 26 fluids appears to be good candidates for an OTEC application. The list of selected working fluids is shown in Table 3, and their technicity indicators are illustrated in Figure 4.

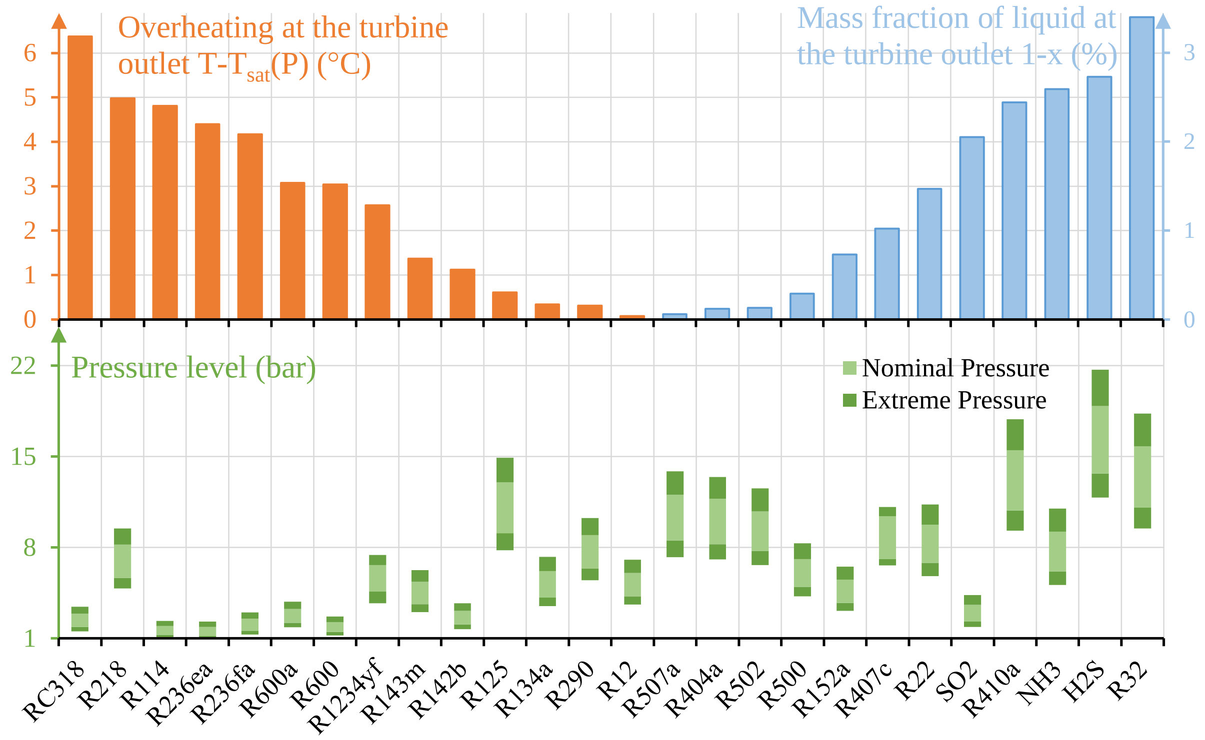


Figure 4 : State of the fluid at the turbine outlet and working pressure range for the 26 fluids of the panel

It is interesting to notice that the two criteria above are correlated. Fluids with the highest operating pressures are also those with the highest liquid quality at the turbine outlet. These fluids are the wet fluids. Most of dry fluids have low operating pressures, but they have a high overheating at the condenser inlet, which will affect cycle performances.

3.3. Security

The ASHRAE standard 34 reference [49] has been chosen as the security indicator. This latter is composed of a letter that indicates the toxicity (from A for non-toxic to C for highly toxic) and a number that indicates flammability (from 1 for non-flammable to 3 for highly flammable). Among the candidates, 14 fluids have the best indicator A1, as shown in Table 3. NH_3 is B2L, that is to say that it is toxic and slightly flammable, and R1234yf is A2L, so it is non-toxic and slightly flammable. Accordingly, R1234yf shows quite good properties for safety considerations, even if it isn't A1.The indicator was not given for H_2S, but it is a toxic and flammable fluid.

3.4 Environmental considerations

A lot of working fluids have been forbidden in order to protect the ozone layer since the Montreal protocol in 1998. Furthermore, as OTEC claim to be an environment-friendly source of energy, it is important to consider the environmental impact of the working fluid. Three indicators have been chosen: the global warming potential (GWP), the ozone depletion potential (ODP), and the atmospheric lifetime (ALT). The GWP represents the impact on the global warming in terms of temperature variation, related to that of a similar mass of CO_2. The ODP is the amount of destruction of the ozone layer, related to that of a similar mass of R11. The ALT is the time in years necessary for a substance to turn over the global atmospheric burden. Values of these three indicators are given in Figure 5. It appears that R1234yf, NH_3, R600a, R600 and R290 have the lowest environmental impact.

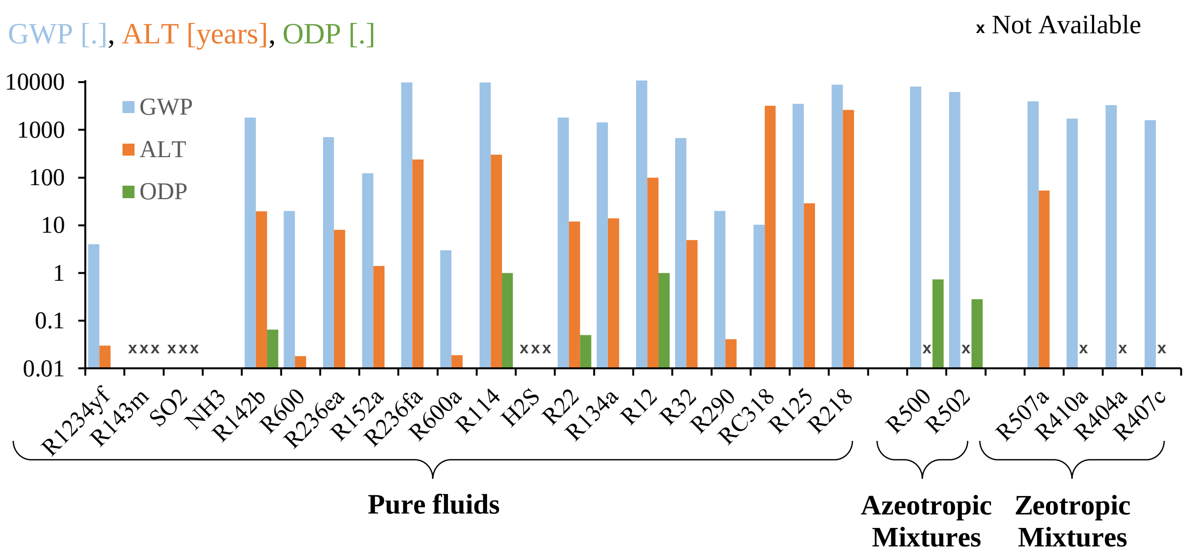


Figure 5. Value of GWP, ALT and ODP for the fluids of the panel

3.5. Thermodynamic performances

According to results given in Table 3, the ranking of the different working fluids depends strongly on the selected criteria. Indeed, considering the specific work w_{net}, NH_3 perform widely better than other fluids (41.98 kJ/kg for NH_3 compared to 14.98 kJ/kg for H_2S in second position). However, considering the thermal efficiency, the gap between different fluids is less important. R143m performs better, but NH_3, R236ea and SO_2 give very close values of thermal efficiency. Considering the net volumic work $w_{net,\,vol}$, H_2S and R32 perform better.

To compare the results, thermal efficiency has been plotted versus volumic net work, as in Figure 6. A Pareto's frontier giving the best fluids is also represented in this figure. Working fluids on this curve are R143m, NH_3, R507a and H_2S. R143m is on the frontier because it has a better η_{th} than NH_3. However, the difference in thermal efficiency between NH_3 and R143m is very small (3.447 % for NH_3 against 3.450 % for R143m), when the volumic work of NH_3 is near twice than R143m. So, R143m do not provide great advantage over NH_3. So, we will not consider R143m in the following of this study.

In conclusion, the best fluids according to the two selected thermodynamic criteria (η_{th} and $w_{net,vol}$) are in first position NH_3, R507a and H_2S. In second position, R134a, R1234yf, R22, R407c, R404a and R32 also show good performances.

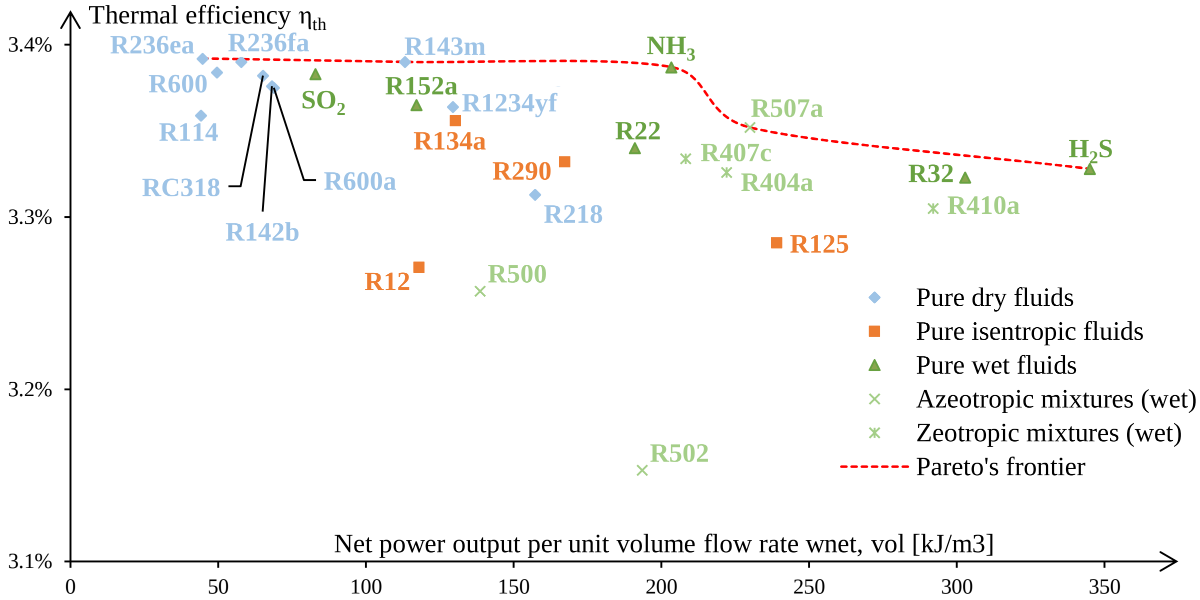


Figure 6. Thermal efficiency versus net volumic work for the selected fluids, and representation of the Pareto's frontier.

3.6. Comparison Synthesis

All fluids in the panel presented were suitable according to the technical criteria. Three working fluids have been chosen by the thermodynamic study, fourteen by the security study, and five by the environmental impact study, as shown in Table 2.

Table 2: Best fluids from thermodynamic, security and environment point of view

Fluids with better thermodynamic performances	Fluids with better safety indicator		Fluids with low ALT, GWP and ODP
NH_3	R507a	R134a	R1234yf
R507a	R236fa	R404a	NH_3
SO2	R218	R12	R600a
	R114	R410a	R600
	R500	RC318	R290
	R22	R125	
	R502	R407c	

Table 3: Properties of selected working fluids and simulation results. The inputs for this simulation are given in Table 1.

	Type of fluid	**State at the turbine outlet [%]**	**ASHRAE**	W_{net} **[kJ/kg]**	$W_{net, vol}$ **[kJ/m³]**	η_{th}
PURE FLUIDS						
R1234yf	isen[1]	Overheated: 2.57°C	A2L	5.57	129.4	3.364%
R143m	isen[1]	Overheated: 1.37°C	n.a.[2]	6.76	113.2	3.390%
SO_2	wet[1]	Diphasic: x=98.0%	B1	12.74	82.9	3.383%
NH_3	wet[1]	Diphasic: x=97.4%	B2L	41.98	203.4	3.387%
R142b	isen[1]	Overheated: 1.12°C	A2	7.46	68.1	3.376%
R600	dry[1]	Overheated: 3.04°C	A3	13.37	49.6	3.384%
R236ea	dry[1]	Overheated: 4.40°C	n.a.[2]	5.89	44.7	3.392%
R152a	wet[1]	Diphasic: x=99.3%	A2	10.27	117.1	3.365%
R236fa	dry[1]	Overheated: 4.17°C	A1	5.53	57.7	3.390%
R600a	dry[1]	Overheated: 3.07°C	A3	12.28	68.8	3.375%
R114	dry[1]	Overheated: 4.81°C	A1	4.79	44.1	3.359%
H_2S	wet[1]	Diphasic: x=97.3%	n.a.[2]	14.98	345.0	3.328%
R22	wet[1]	Diphasic: x=98.5%	A1	6.73	191.0	3.340%
R134a	isen[1]	Overheated: 0.34°C	A1	6.67	130.3	3.356%
R12	wet[1]	Overheated: 0.08°C	A1	4.97	117.9	3.271%
R32	wet[1]	Diphasic: x=96.6%	A2	9.99	302.8	3.323%
R290	isen[1]	Overheated: 0.31°C	A3	12.49	167.3	3.332%
RC318	dry[1]	Overheated: 6.38°C	A1	4.07	65.2	3.382%
R125	isen[1]	Overheated: 0.61°C	A1	4.29	239.1	3.285%
R218	dry[1]	Overheated: 4.98°C	A1	3.08	157.2	3.313%
AZEOTROPIC MIXTURES						
R500	wet[1]	Diphasic: x=99.7%	A1	5.95	138.6	3.257%
R502	wet[1]	Diphasic: x=99.9%	A1	4.55	193.5	3.153%
R507a	wet[1]	Diphasic: x=99.9%	A1	5.32	230.0	3.352%
ZEOTROPIC MIXTURES						
R410a	wet[1]	Diphasic: x=97.6%	A1	7.01	292.0	3.305%
R404a	wet[1]	Diphasic: x=99.9%	A1	5.42	222.1	3.326%
R407c	wet[1]	Diphasic: x=99.0%	A1	7.05	208.2	3.334%

[1] isentropic, wet or dry: type of the fluid depending on the slope of the saturated vapor curve

[2] n.a.: not available

As a result, no fluid meets the three criteria at the same time. However, NH_3 is a very good candidate because it meets good thermodynamic performances and low environmental impact, even if it is toxic. R507a is also a good candidate because it presents good thermodynamic performances, non-toxicity and non-flammability, but its GWP and ALT are high. It is also interesting to notice that R1234yf seems also to be a good compromise because it is in second position for thermodynamic performances, it has very few environmental impacts and isn't toxic and just slightly flammable (A2L). So, in the end, three fluids appear to be the best candidates for OTEC: NH_3, R507a and R1234yf. This selection was made assuming operating conditions and component properties to be constant. A parametric sensitivity analysis will be held in the next part to study the effect of their variations.

4. Parametric sensitivity analysis of the thermodynamic model

4.1 Method

The parametric sensitivity analysis sets out to determine the influence of the variance of each parameter of the model on the results. The most used method found in the literature is the "One Factor At Time" method. This later consists in varying one parameter and keeping the others constant to point out the local sensitivity of the model to this parameter. However, many authors, like Saltelli and Anonni [50] or Campolongo *et al.* [51], consider that this method does not allow a complete comprehension of the model, because it uses many shortcomings and does not take into account the influence of combined effects. Thus, a global sensitivity analysis with the method named ANOVA (ANalysis Of VAriance), by using the Sobol sensitivity indices [52] has been chosen. We consider that every input parameter X_i is a random variable, and the vector of all input parameters $(X_1, \dots, X_p)$ is described by its multidimensional probability distribution. The model then works out the output result $Y=f(X_1, \dots, X_p)$, also considered as a random variable whose distribution depends on that of the parameters X_i. The Sobol sensitivity indices are defined by:

$$S_i = \frac{Var_{X\,i}\left(E_{X_{\sim i}}\left(Y \mid X_i\right)\right)}{Var(Y)} \quad (12)$$

Where X_i is the i-th input parameter and $X_{\sim i}$ represents all parameters excepted X_i. This sensitivity index represents the reduction of the variance of the output Y if the parameter X_i is fixed, that is to say the percentage of the variance of Y due only to the parameter X_i. We can also define the total sensitivity index ST_i as the value of the remaining variance of Y if all parameters but X_i are fixed:

$$ST_i = \frac{E_{X_{\sim i}}\left(Var_{X\,i}\left(Y \mid X_{\sim i}\right)\right)}{Var(Y)} \quad (13)$$

Thus, ST_i represents the percentage of the variance of Y due to the parameter X_i including its interactions with other parameters. In the case of an additive model, $S_i = ST_i$.

In this study, all input parameters are processed to match independent random variables uniformly distributed on the interval $[-1,1]$. Then, Polynomial Chaos Expansion, as described in the work of Sudret or Crestaux *et al*. [53], [54] is conducted. This method is efficient when the number of input parameters is lower than 20 and the function is relatively smooth. This conditions are verified for this study because only 10 parameters are used and the variation of outputs is continuous and regular with the variation of each parameter.

The model is approached by its decomposition in multidimensional polynomial series. To respect the conditions of ANOVA, an orthogonal basis of Legendre polynomials is used, under uniformly distributed variables in $[-1,1]$. The process followed is then:

- Generation of random sets of parameters with respect to the given distribution
- Computation of the model results for each set of parameter
- Determination of the coefficients $a_{i_1,\ldots,i_s}$ of the multidimensional Legendre polynomial (P_{ij}) series that best fit the results (least square method) :

$$f\left(X_1,\ldots,X_p\right)=\sum_{\alpha_{i_1,\ldots,i_s}\in\mathbb{N}^s}^{n} a_{\alpha_{i_1,\ldots,i_s}} P_{\alpha_{i_1,\ldots,i_s}}\left(X_{i_1},\ldots,X_{i_s}\right)=a_1P_1(X_1)+a_2P_2(X_2)+a_{12}P_{12}(X_1,X_2)+\ldots \quad (14)$$

- Calculation of Sobol sensitivity indices: equations 12 and 13 are applied for the result given in equation 14 (for further details, see the work of Crestaux *et al*. [54]).

4.2 Hypothesis

Input parameters of the ORC model are given in Table 4. They are processed with an affine transformation to become variables distributed in $[-1,1]$. Hot seawater temperatures in Reunion Island have been monitored during a ten year period by the ECOMAR Laboratory [55]. This temperature only presents a seasonal fluctuation between 23 °C in winter and 28 °C in summer. In regards to the cold deep seawater temperature, a local study realized by the ARER [56] shows that very weak fluctuations are observed around 5 ° C to 1000 m depth. Other parameters are derived from the OTEC onshore prototype data.

Table 4. Hypothesis of the parametric sensitivity analysis, each variable X_i is uniformly distributed in [-1,1].

Variables	Unit	Mean Value	Variation interval	Transformation
T_{hw}	°C	25.5	[23 ; 28]	$T_{hw} = 25.5 + 2.5X_1$
T_{cw}	°C	5	[4.8 ; 5.2]	$T_{cw} = 5 + 0.2X_2$
ΔT_{over}	°C	1	[0.5 ; 1.5]	$\Delta T_{over} = 1 + 0.5X_3$
ΔT_{sub}	°C	1	[0.5 ; 1.5]	$\Delta T_{sub} = 1 + 0.5X_4$
$\Delta\tilde{T}_{evap}$	°C	4	[2 ; 6]	$\Delta\tilde{T}_{evap} = 4 + 2X_5$
$\Delta\tilde{T}_{cond}$	°C	4	[2 ; 6]	$\Delta\tilde{T}_{cond} = 4 + 2X_6$
η_{turb}	%	0.8	[0.7 ; 0.9]	$\eta_{turb} = 0.8 + 0.1X_7$
η_{pump}	%	0.8	[0.7 ; 0.9]	$\eta_{pump} = 0.8 + 0.1X_8$
ΔP_{cond}	bar	0.15	[0 ; 0.3]	$\Delta P_{cond} = 0.15 + 0.15X_9$
ΔP_{evap}	bar	0.15	[0 ; 0.3]	$\Delta P_{evap} = 0.15 + 0.15X_{10}$

Two output variables are considered:

- thermal efficiency $\eta_{th} = f(X_1, \ldots, X_{10})$ and
- net volumic work $w_{net,vol} = g(X_1, \ldots, X_{10})$.

A maximal polynomial degree of $n = 6$ and a size of the random sample of $N = 1000$ were found to be sufficient to achieve the convergence of the calculation.

4.3 Results

The parametric sensitivity analysis has been conducted for NH_3, R507a and R1234yf. Results are presented in Table 5 and Figure 7.

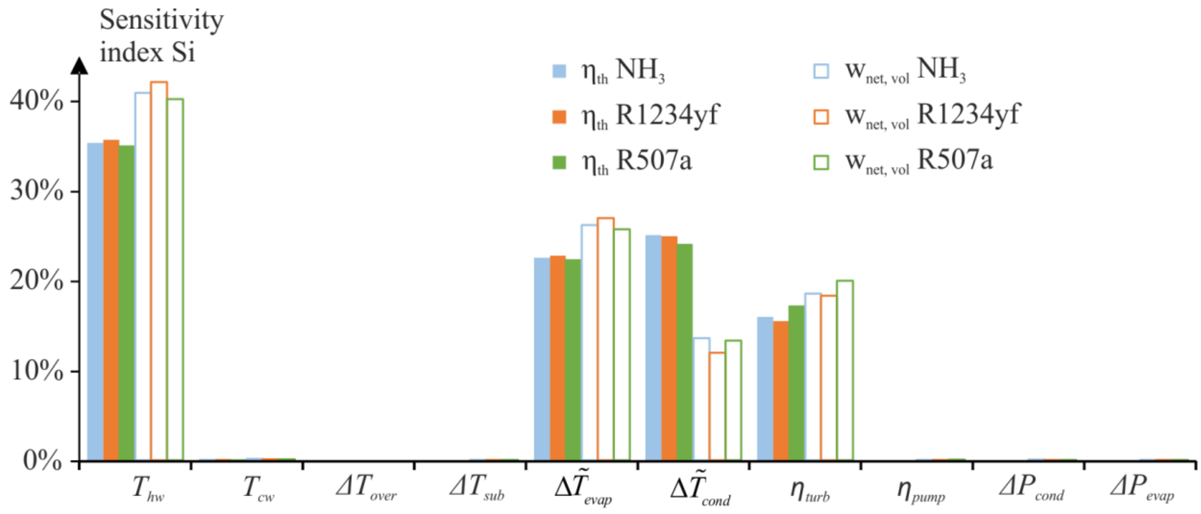


Figure 7. Values of Sobol sensitivity index for the different input parameters for two output variables: the thermal efficiency and the net volumic work.

Table 5. Results of the parametric sensitivity analysis

	NH_3				**R1234yf**				**R507a**			
	η_{th}		***$w_{net,vol}$***		***η_{th}***		***$w_{net,vol}$***		***η_{th}***		***$w_{net,vol}$***	
	Si	***STi***	***Si***	***STi***	***Si***	***STi***	***Si***	***STi***	***Si***	***STi***	***Si***	***STi***
T_{hw}	35.41%	35.61%	40.88%	41.18%	35.75%	35.95%	42.08%	42.39%	35.14%	35.37%	40.16%	40.49%
T_{cw}	0.25%	0.25%	0.14%	0.14%	0.25%	0.25%	0.12%	0.12%	0.24%	0.24%	0.13%	0.13%
ΔT_{over}	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
ΔT_{sub}	0.00%	0.00%	0.01%	0.02%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.01%
$\Delta \tilde{T}_{evap}$	22.66%	22.78%	26.16%	26.35%	22.89%	23.01%	26.94%	27.13%	22.49%	22.63%	25.70%	25.91%
$\Delta \tilde{T}_{cond}$	25.14%	25.27%	13.59%	13.73%	25.05%	25.19%	11.97%	12.11%	24.20%	24.36%	13.32%	13.48%
η_{turb}	16.06%	16.51%	18.53%	19.04%	15.60%	16.05%	18.31%	18.81%	17.32%	17.85%	19.95%	20.55%
η_{pump}	0.03%	0.03%	0.03%	0.03%	0.00%	0.00%	0.00%	0.00%	0.06%	0.07%	0.07%	0.07%
ΔP_{cond}	0.00%	0.00%	0.08%	0.09%	0.00%	0.00%	0.01%	0.01%	0.00%	0.00%	0.01%	0.01%
ΔP_{evap}	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%

Firstly, values of Sobol sensitivity index S_i are very close to those of total sensitivity index ST_i. That means that, considering the domain of definition given for input variables (see Table 4), the model can be considered, in a good approximation as additive (it can be represented as a sum of univariate functions).

Secondly, there are four very influent parameters that stand out in the investigated case: T_{hw}, $\Delta\tilde{T}_{cond}$, $\Delta\tilde{T}_{evap}$ and η_{turb}. Variations of cold seawater temperature are not very influent because, for an OTEC application, it is relatively constant and well known, so this interval of variation is very restricted. The pump has a low influence on the output of the simulations. This can be explained by the fact that the work used in the pump is very low compared to the work produced by the turbine. On the contrary, the influence of the isentropic efficiency of the turbine is very important, because it affects directly the work produced by the ORC. The most interesting results are for variables describing the transformations in HEX.

Indeed, variations of EMTD in both HEX has a strong influence on outputs (even if $w_{net,vol}$ is a little more influenced by the evaporator than by the condenser), but the subcooling in the condenser, the overheating in the evaporator and pressure drops in both HEX have very low values of sensitivity index. That is to say that, when entropic mean temperature differences are fixed, adding an overheating in the evaporator, for example, doesn't change the values of the criteria used for the working fluid comparison, even if this parameters have an impact on the structure of the cycle itself. Therefore, the use of entropic mean temperatures allows to describe the behavior of HEX by just one parameter for fluid comparison, and thus, when this parameter is fixed for every fluid, we can compare fluids in similar conditions of work. This is the advantage of this model in order to carry out a preliminary comparison of working fluids without prejudging the technology of the components.

It is also interesting to notice that the sensitivity analysis gives similar results for the three chosen working fluids. Thus, in the range of variation of the selected parameters, relative performances of this three fluids do not change. Conclusions drawn previously for OTEC are thus valid in the whole domain of variation of the parameters.

5. Conclusion

A model of an Organic Rankine Cycle applied to OTEC is built by using simple parameters ($\Delta\tilde{T}_{evap}, \Delta\tilde{T}_{cond}, \eta_{pump}, \eta_{turb}, ...$) for describing the different components, in order to be applicable to every kind of technology and to compare performances of different kinds of fluids in similar conditions. For this purpose, heat exchangers are described by the entropic mean temperature difference parameter. This model is used to establish the behavior of 26 fluids, using experimental measurements of an OTEC onshore prototype as input parameters. A comparison of these fluids is then carried out by considering various criteria. In particular, for thermodynamic performances, we use a plot with the representation of a Pareto's frontier on which the choice is based. A parametric sensitivity analysis was then carried out in order to understand the behavior of the model and the importance of each parameter. The main results of this study are:

- In order to compare pure fluids and mixtures, the entropic mean temperature difference in HEX allows to draw the cycle with a reduced number of hypothesis and is more representative of similar working conditions of the different fluids than traditional parameters such as the output temperature difference.

- There is no fluid that meets at the same time great thermodynamic performances, easy implementation, safety and low environmental impacts. However, NH_3 and R507a seem to be good candidates because they both have good thermodynamic performance (thermal efficiency and volumic work). Moreover, NH_3 has very low environmental impacts (GWP, ODP, ALT), but it is toxic and mildly flammable (B2L). R507a is neither toxic nor flammable, but it has high values of GWP and ALT. R1234yf is also a good candidate, even if it ranks second of the thermodynamic study, it is nontoxic unlike NH_3, and it has very low environmental impacts.
- The parametric sensitivity analysis revealed that, in the chosen domain of input parameters, the model is approximatively additive and the most relevant parameters are T_{hw}, $\Delta\tilde{T}_{evap}$, $\Delta\tilde{T}_{cond}$, and η_{turb} for this application.

This study will be useful for helping in choosing the working fluid of an ORC in a preliminary study preceding the design of the components.

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Nomenclature

		<u>Subscripts</u>	
T	Temperature [K]	hw	Hot Water at the evaporator inlet
η	Efficiency [%]	cw	Cold Water at the condenser inlet
q	Specific heat transfer [$J.kg^{-1}$]		
w	Specific work [$J.kg^{-1}$]	1	Evaporator inlet
h	Specific enthalpy [$J.kg^{-1}$]	2	Turbine inlet
s	Specific entropy [$J.\ kg^{-1}.K^{-1}$]	3	Condenser inlet
<u>Specific notations</u>		4	Pump inlet
$\Delta\tilde{T}$	Entropic mean temperature difference [K]	is	Isentropic
		evap	Evaporator
w_{net}	Net specific work of the cycle [$J.kg^{-1}$]	cond	Condenser
$w_{net, vol}$	Total volumic work of the cycle [$J.m^{-3}$]	pump	Pump
<u>Acronyms</u>		turb	Turbine
ORC	Organic Rankine Cycle	vol	Volumic
OTEC	Ocean Thermal Energy Conversion	th	Thermal
EMTD	Entropic Mean Temperature Difference	over	Overheating
GWP	Global Warming Potential	sub	Subcooling
ODP	Ozone Depletion Potential		
ALT	Atmospheric Lifetime		