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Article

## Exergy Assessment of Recovery Solutions from Dry and Moist Gas Available at Medium Temperature

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**Abstract:** The Agence Nationale de la Recherche (ANR-EESI) ENERGY ReCOvery from Low Temperature heat sources (ENERCO\_LT) project is a waste heat recovery project that aims to reduce energy consumption in industrial gas production sites, by producing electrical power from exothermic processes discharges at low and medium temperature. Two promising thermal sources, consisting of: (i) almost dry gas flow at 165 °C and (ii) moist gas flow at 150 °C with a dew point at 60 °C, were then investigated. In this paper, the challenge was to discern suitable recovery solutions facing resource specificities and their thermodynamic constraints, in order to minimize the overall exergy destruction, *i.e.*, to move up the exergy efficiency of the entire system. In this spirit, different designs, including Organic Rankine Cycles (ORCs) and CO<sub>2</sub> transcritical cycles, operating as simple and cascade cycles, were investigated. Combined exergy analysis and pinch optimization was performed to identify the potential of various working fluids, by their properties, to overcome the global irreversibility according to the studied resource. Supercritical parameters of various working fluids are investigated too, and seem to bring promising results regarding system performances.

**Keywords:** thermodynamic optimization; exergy; pinch; ORC; subcritical cycles; transcritical cycles; cascade

**Nomenclature:**

$h$	specific enthalpy [kJ/kg]	$HFC$	hydrofluorocarbon
$s$	specific entropy [kJ/kg K]	$HFO$	hydrofluoro-olefin
$ex$	specific exergy [kJ/kg]	$GWP$	Global Warming Potential
$\dot{E}x$	exergy flow [kW]		
$\dot{W}$	mechanical power [kW]	<i>Subscripts</i>	
$\Phi_{in}$	heat flow added to vapour generator [kW]	c	critical
$\Phi_{out}$	heat flow rejected from cycle [kW]	o	ambient
$\Phi'_{out}$	heat flow non recovered [kW]	p	pump
$\theta$	Carnot factor	t	turbine
$T$	temperature [°C]	vg	vapour generator
$P$	pressure [bar]	cd	condenser
$\dot{m}$	mass flow rate [kg/s]	f	flue gases
$\eta$	efficiency	d	destroyed
$\eta_{ex}$	cycle exergy efficiency	s	isentropic
$\eta_{ex,g}$	global exergy efficiency	g	global
$C$	volume capacity [kJ/m <sup>3</sup> ]	L	low
$TIT$	turbine inlet temperature [°C]	H	high
$TET$	turbine exhaust temperature [°C]		
$ORC$	Organic Rankine Cycle	<i>Superscripts</i>	
		~	equivalent

**1. Introduction**

Recent years have seen a particular focus on renewable energies such as solar, wind energy, biomass, geothermal and waste heat recovery from industrial processes. In addition to their economic advantages from reducing fossil fuel consumption, the use of these energies contributes to the reduction of atmospheric emissions of greenhouse gases.

Exothermic processes offer more than final products for which they are incurred, exergy flows in excess from the effluents. These quantities of exergy have not been subject of transfer or conversion, or even destruction during the previous evolutions and therefore remain in thermal form present in dry or moist flue gases before they are totally destroyed through exhaust or via gas coolers when the effluent is re-employed in downstream process.

With regards to the specificities of release conditions of the resource, its molar composition and the thermodynamic constraints that it may have, no fluid can be presented *a priori* as the best recovery solution, especially when comparing dry exergy resources and highly moist ones. Therefore, as a first step, available resources will be characterized.

Liu *et al.* [1] have studied analytically the influence of the working fluid, by its properties and its operating conditions, on system performances and highlighted, when calling to thermodynamic optimization, the interest of focusing studies on global efficiency of the whole system rather than thermal efficiency of the working cycle. Other studies, performed by Madhawa *et al.* [2] and Kanoglu *et al.* [3] are based on exergy approaches to properly parameterize ORCs for geothermal applications. Schuster *et al.* [4] have pointed out that R-245fa, a hydrofluorocarbon (HFC), is suitable for a power plant recovering heat from a thermal source at an initial temperature of 210 °C. This fluid is studied in this paper for lower hot source inlet levels and compared to other alternatives.

## 2. Resources Characterization

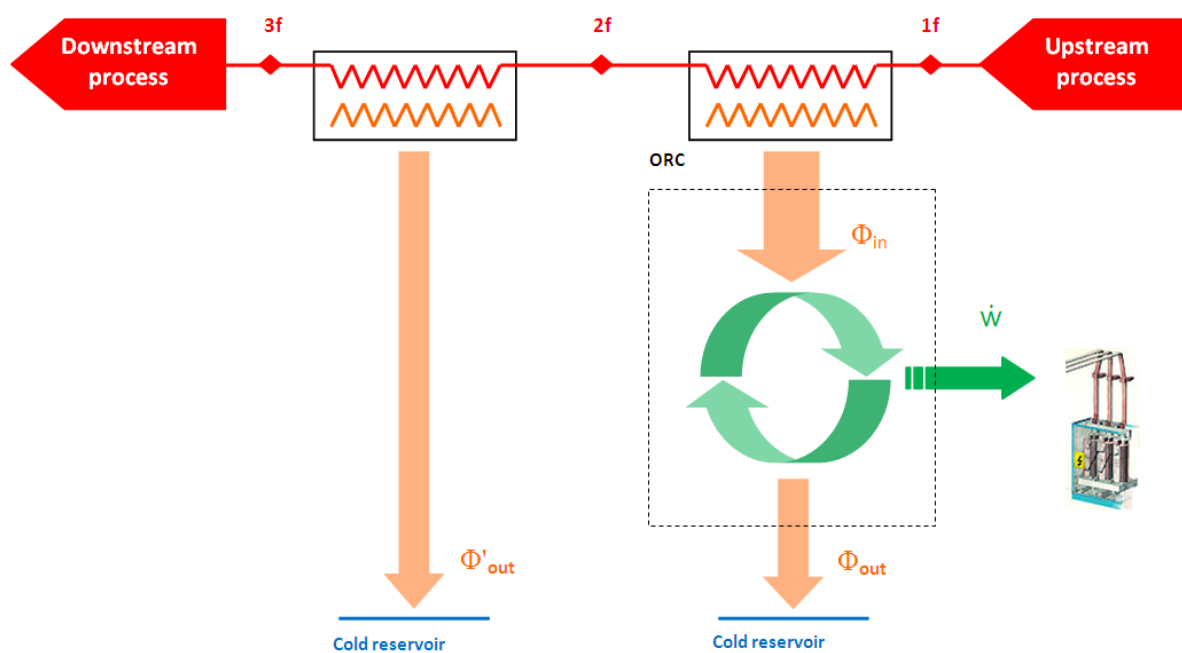
Waste heat recovery related to ENERCO\_LT project covers various gas production plants, such as air separation units, Steam Methane Reforming plants (SMR) and oxy-combustion processes.

When considering an ordinary recovery system, as shown in Figure 1a, the overall available resource is defined as bounded by the upstream process outlet 1f and the downstream process inlet 3f. Overall exergy resources are determined according to the cooling conditions of effluents and their molar compositions as expressed below:

$$\dot{E}x_{3f1f} = \dot{m}_f(ex_{1f} - ex_{3f}) \quad (1)$$

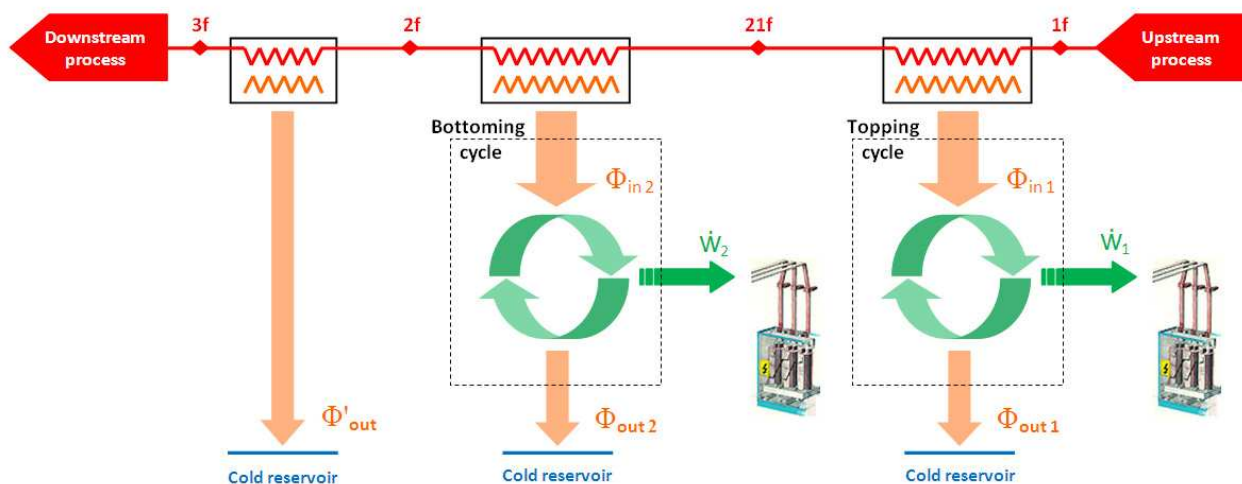
Two resources are considered, summarized in Table 1. Exergy calculations take as reference the ambient temperature  $T_o$  of 15 °C.

**Figure 1.** (a) Scheme of one cycle recovery process; (b) Scheme of two-cycle cascade recovery process.



(a)

Figure 1. Cont.



(b)

Table 1. Resource characteristics.

Resource	$T_{1f}$ [°C]	$P$ [bar]	Water molar fraction [%]	Mass flow rate [kg/s]	Dew point [°C]	$\dot{E}x_{3f1f}$ [kW]
almost dry	165	25	2	152.2	75	4950
moist	150	1	20	130.2	60	6148

The first resource, with low humidity content, is cooled from 165 °C to 25 °C and shows an exergy flow about 4.9 MW thanks to a high mass flow rate. The second resource, highly moist, is cooled from 150 °C to 25 °C and shows an exergy flow about 6.1 MW thanks to an additional latent heat provided by the condensation of water vapour at low temperature.

From these exergy resources, work production can be evaluated from the exergy efficiency of the engine cycles  $\eta_{ex}$ . For a single recovery engine cycle (Figure 1a):

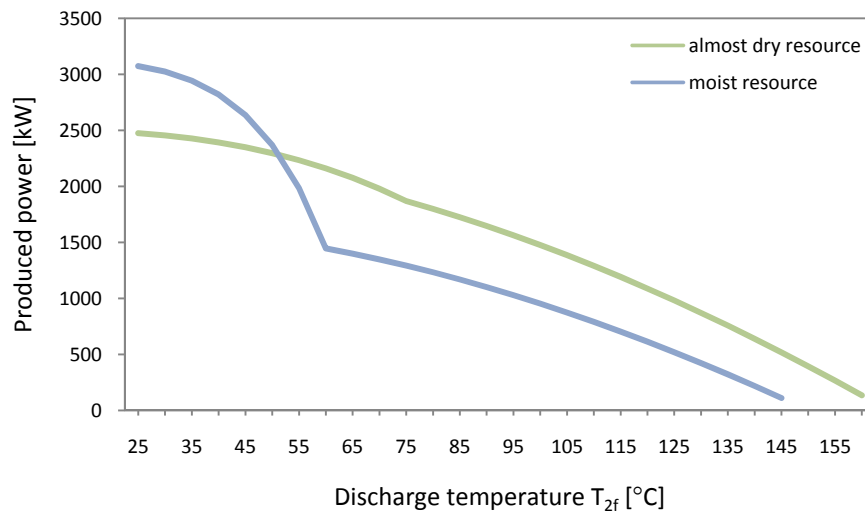
$$\eta_{ex} = \dot{W} / \dot{E}x_{2f1f} \tag{2}$$

For a cascading recovery engine cycle (Figure 1b):

$$\eta_{ex,1} = \dot{W}_1 / \dot{E}x_{21f1f}, \eta_{ex,2} = \dot{W}_2 / \dot{E}x_{2f21f} \tag{3}$$

Figure 2 estimates the production of work according to the discharge temperature  $T_{2f}$  for a fixed exergy efficiency of the cycle equal to 50%. The representation shows that the best global performance is achieved with low discharge temperature  $T_{2f}$ . Moreover, it can be seen that condensing process significantly increases the exergy resource, and then the work production. For the moist resource, the change of slope when crossing the dew point is particularly important.

Nevertheless, this first study does not take into account the fitting between the cooled flow (the resource) temperature profile and the working fluid temperature profile which could be difficult to match with a single recovery engine cycle. As a consequence, 50% exergy efficiency could be not reachable with such a cycle, and would require a cascading cycle (Figure 1b); the first one working on the right of the dew point ( $T_{21f} \approx T_{dew}$ ), and the second one taking advantage of the condensing process.

**Figure 2.** Produced power calculated for 50% cycle exergy efficiency.

### 3. Exergy Analysis

It is well known that exergy efficiency of an engine can be expressed according to the exergy destructions  $\dot{E}x_{d,i}$  of the constituting components: heat exchangers, pumps, turbines, ducts, *etc.*

For a single cycle, exergy efficiency (Equation 2) can also be written as:

$$\eta_{ex} = 1 - \sum_i \frac{\dot{E}x_{d,i}}{\dot{E}x_{2f1f}} \quad (4)$$

This form is particularly interesting because it emphasizes which processes are mainly responsible of the exergy efficiency degradation. In a vapour power plant, the irreversibilities are generally qualified as internal or external irreversibilities. The internal exergy destruction is caused by:

- friction forces at the origin of pressure losses in the internal structures of the system, where the work of these forces is transformed into heat,
- internal heat transfer at finite difference temperature, in case of internal heat recovery.

The external irreversibilities are caused by:

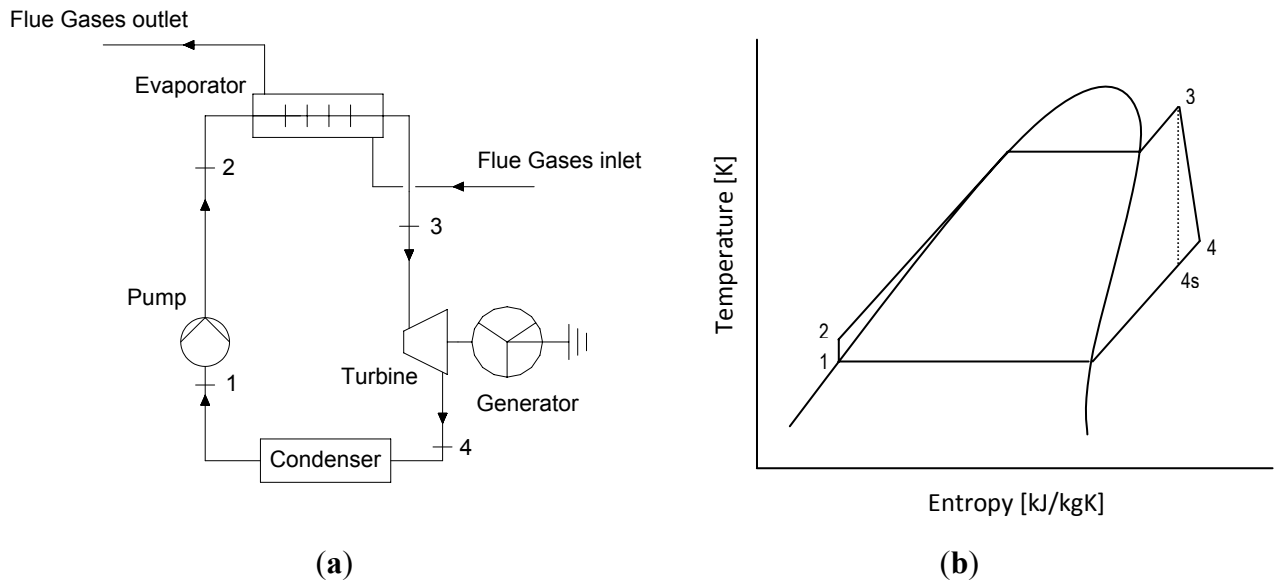
- heat transfers at finite difference temperatures between the working fluid and external hot or cold sources,
- mechanical transfer of work.

The cycle exergy destruction covers the internal and external irreversibilities that occur inside the working cycle, basically in feed pump, vapour generator, turbine, condenser and eventually the regenerator when adopted [5]. Moreover, it is denoted by exergy loss, the irreversibility occurring outside the working cycle; that is the exergy flow  $\dot{E}x_{3/2f}$  excluded from the recovery process.

The evolution of working fluid into the investigated cycle can be summarized in four unitary operations as shown in Figure 3. The working fluid leaves the condenser as a saturated liquid at temperature  $T_l$  and condensation pressure  $P_L$  (point 1), then it is compressed into a feed pump to an evaporation pressure  $P_H$  (point 2) with a proper isentropic efficiency  $\eta_{s,p}$ . At the outlet of the pump, the fluid is heated at constant pressure in the evaporator until it becomes saturated in vapour or

superheated, and reaches  $T_3$  temperature (point 3). The vapour is then expanded in a turbine to the condenser pressure  $P_L$  (point 4). During expansion, the fluid delivers mechanical work with a proper isentropic efficiency  $\eta_{s,t}$ . Finally, the fluid passes through the condenser releasing heat at constant pressure until it becomes saturated in liquid.

**Figure 3.** Simple ORC. (a) Schematic diagram; (b) ( $T$ - $s$ ) diagram.



For each unitary process (*i.e.*, for each component), thermal and/or mechanical power and exergy destruction is evaluated from the energy and exergy balances, assuming stationary regime.

Pump (1 to 2): Assuming adiabatic compression, energy and exergy balances can be written as:

$$\dot{W}_p + \dot{m}(h_1 - h_2) = 0 \tag{5}$$

$$\dot{W}_p + \dot{m}(ex_1 - ex_2) - \dot{Ex}_{d,p} = 0 \tag{6}$$

Isentropic efficiency is defined as the ratio of ideal mechanical power (*i.e.*, reversible pump) and actual mechanical power:

$$\eta_{s,p} = \frac{\dot{W}_{p_s}}{\dot{W}_p} = \dot{m} \frac{h_{2s} - h_1}{\dot{W}_p} \tag{7}$$

The power consumed by the pump then becomes:

$$\dot{W}_p = \frac{\dot{m}(h_{2s} - h_1)}{\eta_{s,p}} \tag{8}$$

Equation 5 gives then the specific enthalpy of point 2 (which is then completely defined, pressure  $P_2$  being known). Equation 6 gives the exergy destruction by the pumping process:

$$h_2 = h_1 + (h_{2s} - h_1)/\eta_{s,p} \tag{9}$$

$$\dot{Ex}_{d,p} = \dot{m}(ex_2 - ex_1) - \dot{W}_p = \dot{m}T_o(s_2 - s_1) \tag{10}$$

Vapour generator (2 to 3): Isobaric transformation is assumed for the working fluid. For the hot source, gas stream is cooled to an outlet temperature  $T_{2f}$ , taking as design parameter. Energy and exergy balances are given by:

$$\dot{m}_f(h_{1f} - h_{2f}) + \dot{m}(h_2 - h_3) = 0 \quad (11)$$

$$\dot{m}_f(ex_{1f} - ex_{2f}) + \dot{m}(ex_2 - ex_3) - \dot{E}x_{d,vg} = 0 \quad (12)$$

Introducing the equivalent temperature of transformation (2 to 3) and (1f to 2f), and the heat power transferred from the hot gas to the cycle  $\Phi_{in}$ :

$$\phi_{in} = \dot{m}_f(h_{1f} - h_{2f}) = \dot{m}(h_3 - h_2) \quad (13)$$

$$\tilde{T}_{1f2f} = \frac{\Delta h_{1f2f}}{\Delta s_{1f2f}} \quad (14)$$

$$\tilde{T}_{23} = \frac{\Delta h_{23}}{\Delta s_{23}} \quad (15)$$

Exergy destruction in the vapour generator can be expressed by:

$$\dot{E}x_{d,vg} = \phi_{in} \cdot (\tilde{\theta}_{1f2f} - \tilde{\theta}_{23}) \quad (16)$$

with:

$$\tilde{\theta}_{ij} = 1 - \frac{T_o}{\tilde{T}_{ij}} \quad (17)$$

Turbine (3 to 4): Except for the isentropic efficiency definition, energy and exergy balance are similar to those write to the pump. For a turbine, isentropic efficiency is defined as the ratio of actual mechanical power and ideal mechanical power:

$$\eta_{s,t} = \frac{\dot{W}_t}{\dot{W}_{t,s}} = \frac{\dot{W}_t}{\dot{m} \cdot (h_{4s} - h_3)} \quad (18)$$

Then, actual power, specific enthalpy  $h_4$  and exergy destruction are:

$$\dot{W}_t = \dot{m}(h_{4s} - h_3) \times \eta_{s,t} \quad (19)$$

$$h_4 = h_3 + (h_{4s} - h_3) \times \eta_{s,t} \quad (20)$$

$$\dot{E}x_{d,t} = \dot{W}_t + \dot{m}(ex_3 - ex_4) = \dot{m} T_o (s_4 - s_3) \quad (21)$$

Condenser (4 to 1): Isobaric operation is assumed, and condensing heat is transferred to cooling water, supposed at exergy reference temperature  $T_o$ . Energy and exergy balances are:

$$\phi_{out} + \dot{m}(h_4 - h_1) = 0 \quad (22)$$

$$\theta_o \phi_{out} + \dot{m}(ex_4 - ex_1) - \dot{E}x_{d,cd} = 0 \quad (23)$$



As  $\theta_0$  is 0, this yields:

$$\phi_{out} = \dot{m} (h_1 - h_4) \quad (24)$$

$$\dot{E}x_{d,cd} = \dot{m}(ex_4 - ex_1) \quad (25)$$

Equivalent temperature can also be introduced here:

$$\tilde{T}_{41} = \frac{\Delta h_{41}}{\Delta s_{41}} \quad (26)$$

and exergy destruction in the condenser could be expressed as follows:

$$\dot{E}x_{d,cd} = \tilde{\theta}_{14} \phi_{out} \quad (27)$$

The total exergy destroyed into the working cycle is equal to the sum of the irreversibilities generated within each component:

$$\dot{E}x_d = \sum_i \dot{E}x_{d,i} \quad (28)$$

Finally, the global destruction is equal to the sum of the exergy destroyed inside and outside the cycle:

$$\dot{E}x_{d,g} = \sum_i \dot{E}x_{d,i} + \dot{E}x_{3f2f} \quad (29)$$

and the global exergy efficiency  $\eta_{ex,g}$  can be written as:

$$\eta_{ex,g} = 1 - \frac{\dot{E}x_{d,g}}{\dot{E}x_{3f1f}} \quad (30)$$

According to the Second Law of Thermodynamics, within a system having real evolutions, it is impossible to convert the whole available thermal energy into useful work. The contribution to the exergy destruction in the system differs from one component to another; it is dictated in part by the properties of the employed fluid and in another part by the evolution conditions of this fluid within components of the system. Exergy analysis shows also that it is not recommended to optimize separately the components as if each treated process was isolated from the others. Thus, in order to reach a final design with minimum overall irreversibilities, the working fluid should be selected with care and operating conditions shall be subject to systemic optimization based on simultaneous analysis of all the alterations produced.

#### 4. Static Studies of Recovery Solutions

Calculation tools for recovery process simulation and optimization were created and developed according to the distinctive investigated designs and in convenience with the operating static regimes (subcritical and supercritical), from the Prosim Plus 3.1 simulator [6,7]. The working fluid properties are calculated using REFPROP 8.0 developed by the National Institute of Standards and Technology [8].

The challenge of technico-economic optimization consists in developing sensitivity analysis on cost variations around the pinch while thermodynamic optimization of energy systems requires that the

pinch be as small as possible by bringing system near a limit case. Following calculations have been done for a quasi-limit case of 10 K pinch in vapour generator without incurring additional need for heat in the endothermic zone. Isentropic efficiencies of feed pump and turbine are set respectively to 0.9 and 0.85. As for cooling conditions, cold isobar has been fixed to a liquid saturation temperature of 25 °C.

#### 4.1. Results and Discussion for Almost Dry Resource

The existence in itself of pinch is at the origin of exergy destruction accompanying the cooling of hot gases. Although a minimized pinch contributes to a better cooling, however its location on the composite curve remains a sensitive point able to degrade global performances of the system.

When studying a working cycle using R-245fa, Figure 4a shows that the variation of the vaporization pressure (leading to the variation of pinch location on the composite curves and therefore the discharge temperature  $T_{2f}$ ) does not affect the cycle exergy destruction and the exergy loss in the same manner, *i.e.*, if it reduces the exergy loss outside of the working cycle, it amplifies the exergy destruction inside of it and vice versa. As the final objective is to reduce the overall irreversibility of the entire system, a compromise should be found between these two irreversibilities reductions.

Otherwise, in Figure 4b, the global exergy efficiency shows a maximum value obtained at a subcritical pressure, below which the cycle exergy destruction appears dominant and above which, the exergy loss  $\dot{E}x_{3/2f}$  becomes dominant. Such significant optimum corresponds to an appropriate phase change temperature, not very high and not close to the hot source inlet temperature.

**Figure 4.** R-245fa global performance from almost dry resource. (a) Irreversibilities diagram; (b) Global exergy efficiency behavior.

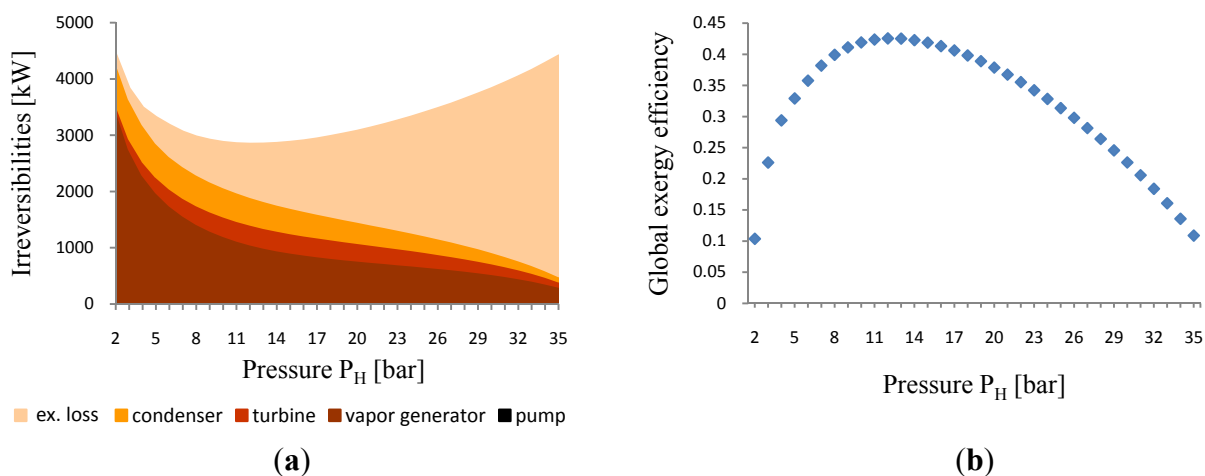


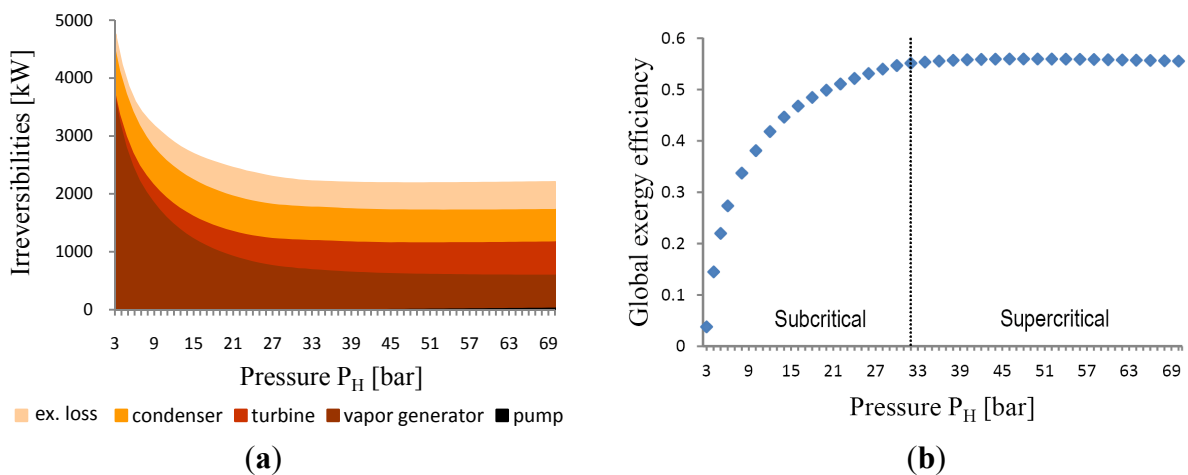
Figure 4 clearly illustrates the contribution of exergy analysis in optimization problems. As for the choice of the working fluid to use, this will depend on its thermophysical properties and on the resource requirement, mainly the critical temperature, latent heat and the slopes of both saturation lines on the ( $T-s$ ) diagram.

As seen in Figure 6a, R-245fa cannot be regarded as an appropriate solution since its critical temperature is slightly lower than the hot source inlet temperature. This prevents adequate temperature

matching between the flue gases and the working fluid. It results in an acute pinch at the end of the preheating zone. In this case, and because of the high critical temperature, systemic optimization seeking to maximize the global efficiency leads to a ratio between the vaporization latent and sensible preheating heat close to one. However, even at the optimum, both cycle exergy destruction and exergy loss remain important.

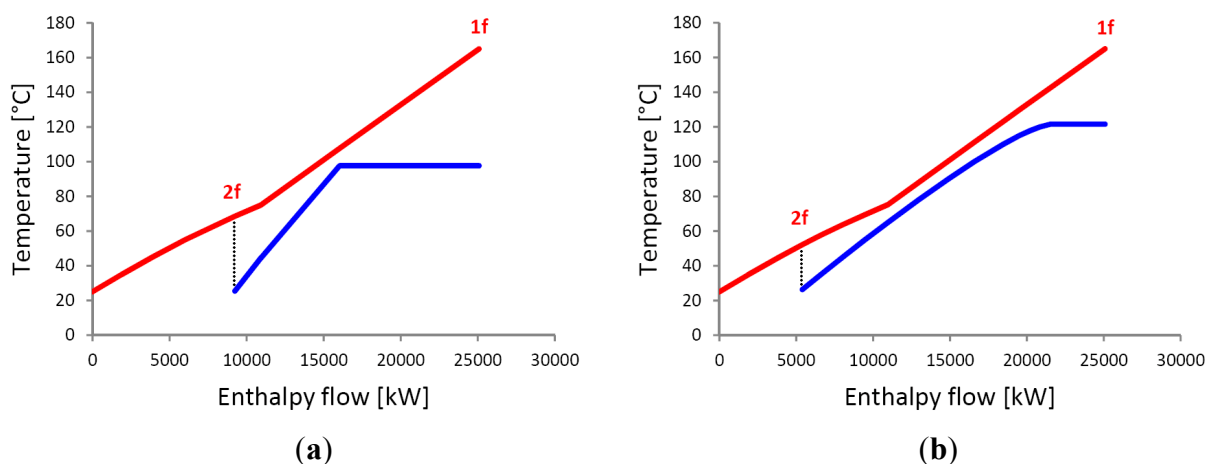
As seen in Figure 6b, R-236fa is identified as an interesting working fluid according to the almost dry resource. Thanks to its properties, this fluid leads to a better temperature matching between the hot and cold flows with a high temperature level at the entrance to turbine. In this case, sensible preheating, far exceeding vaporization latent heat, leads to high subcritical temperature, close to the critical one, limiting therefore the vapour generator irreversibilities.

**Figure 5.** R-236fa global performance from almost dry resource. (a) Irreversibilities diagram; (b) Global exergy efficiency behavior.



Moreover, it can be seen from Figure 5, that the maximum value of global exergy efficiency is spotted at supercritical pressure where the cycle reaches a triangular shape. In this case, the optimum issue is no longer of such significance, especially when operating at high supercritical pressures. Table 2 indicates that R-236fa, leads to an increase of the optimal global efficiency of only 2% compared to subcritical design *i.e.*, net power gain of 62 kW.

**Figure 6.** Almost dry resource composite curves. (a) R-245fa solution; (b) R-236fa solution.



Using dry and isentropic fluids with high boiling point is interesting because they will not require superheat, especially when this latter is able to degrade global system performances by amplifying the exergy loss. For that reason, both subcritical cycles using the R-245fa and R-236fa do not foresee superheat. As for transcritical cycle, the rise of vapour temperature increases the exergy loss and should be subject to exergy analysis.

The ORC employing R-236fa, even proved as the better solution for the recovery problem, cannot be used in practice, due to its high Global Warming Potential value (GWP). Despite a critical temperature slightly outside the appropriate range, R-1234yf, an environmentally friendly hydrofluoro-olefin (HFO), is a good compromise between environmental impact and performance and is applicable for the dry resource recovery process. Performances of subcritical and transcritical cycles using this fluid are summarized in Table 2.

**Table 2.** Almost dry resource: cycle performances.

Fluid	GWP	$P_C$ [bar]	$T_C$ [°C]	$P_L$ [bar]	$P_H$ [bar]	TIT [°C]	TET [°C]	$T_{2f}$ [°C]	$C$ [kJ/m <sup>3</sup> ]	$W$ [kW]	$\eta_{ex}$ [%]	$\eta_{ex,g}$ [%]
R-245fa	950	36.5	154	1.4	12	97.7	43.3	68.6	2248	2107	52.5	42.6
R-236fa	9400	32	124.9	2.7	30	121.6	33.9	52.2	9801	2710	59.7	54.7
				2.7	48	143.4	29.9	52.8	19,741	2772	61.2	56
R-1234yf	4	32.6	94.8	6.7	32	95.6	25.2	44.9	5352	2376	50.6	48
				6.7	70*	142.6	37.5	54.7	16,440	2676	59.8	54.1

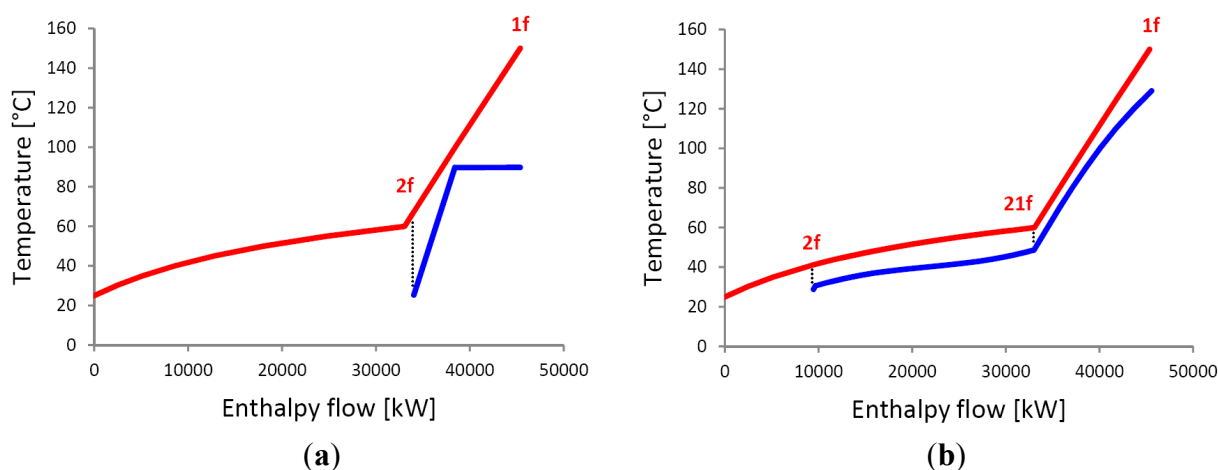
\* This value does not correspond to the maximal performance but has been considered as a limit of the acceptable pressure.

#### 4.2. Results and Discussion for Moist Resource

When using R-245fa as working fluid, the flue gases of both resources (dry and moist) are released at approximately the same temperature (68 °C). However, lower global exergy efficiency is obtained from moist flue gases recovery, since important exergy content is released at a low temperature of 60 °C (Figure 7a).

On the other hand, an ORC, subject to a judicious choice of the working fluid basing on its thermophysical properties and correctly optimized by identifying suitable working conditions, seems to complete the requirements of the almost dry resource but it is not revealed sufficient in the case of the moist resource, since the dew point of this latter leads to a breakage on the shape of the hot composite curve.

A two-cycle cascade as presented in Figure 1b is able to raise global performances. The best solution is the one that results in better gases cooling conditions with highest cycle exergy efficiencies in the two regions, upper and lower, separated by the dew point. The solution presented in Figure 7b consists of two transcritical cycle cascade using R1234yf in the topping one and carbon dioxide in the bottoming one, and leads to a minimum exergy destruction, in both cycles heat exchangers. However, this solution presents a technological constraint since the bottoming cycle, at the optimum, is operated at a high supercritical pressure of 90 bar (Table 3).

**Figure 7.** Moist resource composite curves. (a) R-245fa solution; (b) R-1234yf + CO<sub>2</sub> solution.**Table 3.** Moist resource: cycle performances.

System	Fluid	$P_L$ [bar]	$P_H$ [bar]	$TIT$ [°C]	$TET$ [°C]	$T_{21f}/T_{2f}$ [°C]	$C$ [kJ/m <sup>3</sup> ]	$W$ [kW]	$\eta_{ex}$ [%]	$\eta_{ex,g}$ [%]
Single cycle	R-245fa	1.4	10	89.7	41.3	67.3	1679	1403	50.9	22.8
Cascade	R-1234yf	6.7	60	129	25.2	58.6	13,998	1876	58.6	42
	CO <sub>2</sub>	64.3	90	48.6	25.8	41.1	2435	706	29.8	

## 5. Conclusions

Systemic optimization by extension of pinch method, although it correctly optimizes the system, does not adapt it to the specificities of the available resource, since the fluid has influence on system performance not only by its operating conditions, but also by its thermophysical properties.

It has been demonstrated that, when facing a recovery problem, *a priori* bets on designs and fluids cannot be made before assessing their adequacy to the requirements of the particular problem. Based on the First and Second Law of Thermodynamics, the optimized solution can be identified via an appropriate design, an adequate working fluid and under suitable working conditions, able to overcome pinch problem dictated by fluid properties and thermodynamic constraints imposed by the resource itself. However, other constraints, predominately technological and environmental, come into consideration and have to be included in the optimization process.

In particular, it can be noted that the presence of contaminants and the possible condensation process involved for the moist resource will require high quality materials for the heat exchangers. Thus, an economic analysis is very important after the thermodynamically optimized configuration is set. Furthermore, a multi-objective optimization would be interesting to look at the trade-offs of the system between efficiency and cost.

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