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ANALYSIS OF THE POTENTIAL OF CO_2 BASED MIXTURES TO IMPROVE THE EFFICIENCY OF COGENERATIVE WASTE HEAT RECOVERY POWER PLANTS

Ettore Morosini*
Politecnico di Milano
Milano, Italy

Michele Doninelli
Università degli studi di Brescia
Brescia, Italy

Dario Alfani
Politecnico di Milano
Milano, Italy

Marco Astolfi
Politecnico di Milano
Milano, Italy

Gioele Di Marcoberardino
Università degli studi di Brescia
Brescia, Italy

Giampaolo Manzolini
Politecnico di Milano
Milano, Italy

ABSTRACT

The waste heat potentially available from a wide range of industrial processes still represents a significant fraction of the primary energy consumption related to the processes.

Some of the most energy intensive processes can be categorized in the iron, steel and glass production, the fine chemical industry, and the production of non-ferrous materials such as cement, polymers, paper or in the textile industry. Of the overall thermal energy rejected in the environment, a part of it is feasibly exploitable from a technical and economical point of view in waste heat recovery plants. This work proposes innovative solutions for waste heat recovery cycles working with sCO_2 cycles and transcritical cycles adopting CO_2-mixtures. As the heat rejection from these cycles is non-isothermal, these power plants are particularly suitable to be used in CHP configuration, therefore transferring heat to a stream of pressurized water at high temperature, up to 200°C.

When a waste heat source available at 450°C is considered, assuming a stack temperature of 125°C, the proposed sCO_2 power cycle can convert around 12% of the thermal input in electricity and 87% in useful heat above 60°C, while a cycle working with the CO_2+Acetonitrile mixture can deliver 15.5% of the thermal input in electricity while still recovering the remaining more than 80% in useful heat above 60°C.

CO_2 based mixtures are therefore suggested for power cycles in CHP configuration to reach nominal electric efficiencies higher than sCO_2, avoiding the consumptions of natural gas to produce the same amount of electricity and heat with separated systems.

INTRODUCTION

All across the developed and developing countries an increasing amount of waste heat from industrial processes can be recovered in Waste Heat Recovery (WHR) plants. Especially for small scale applications, these plants normally consist of power cycles, as the Organic Rankine Cycles (ORC), producing electric power by cooling down the exhaust gases released in the environment as much as possible, before releasing them at the stack [1]. The state of the art of ORCs can be identified in subcritical cycles operating with organic fluids, allowing for maximum temperatures decisively lower than the ones achieved in steam cycles. ORCs can be designed as cogeneration units in Combined Heat and Power (CHP) plants by increasing the condensation temperature, entailing a non-negligible penalization of electric efficiency, while, thanks to their flexibility, can switch to pure electric mode when heat is not required by the thermal user.

As a matter of fact, considering the soaring prices of natural gas and other fuels for conventional fossil fuels-based boilers, alternative solutions to produce low temperature heat are considered increasingly attractive. The potential of supercritical carbon dioxide (sCO_2) power cycles for electricity generation in the industrial WHR sector has been already investigated in several works [2–4]. However, differently than ORC, sCO_2 power cycles do not show iso-thermal heat rejection from the cycle, and therefore they can be employed in CHP plants for WHR applications without a strong penalization in electrical efficiency, without any bleeding, unlike steam cycles. The produced useful heat from the sCO_2 cycle, in the 60-200°C range, can be released in part at low temperature for space heating in district heating networks and in part exploited at higher temperature as industrial process heat, adaptable to a variety of applications such as drying, carbon capture with amines, sterilization or thermal desalination. In the US this technological solution was proposed to the market by Echogen Power Systems [5], which manufactured and commercialized sCO_2-based systems also in CHP configuration.

In addition to sCO_2 cycles, transcritical cycles adopting CO_2-based mixtures as working fluid are also investigated in this work for CHP applications: a more innovative family of power cycles gaining ground in the last few years among various

* ettore.morosini@polimi.it

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literature works regarding concentrated solar power, as in the SCARABEUS project [6] and the DESOLINATION project [7], two H2020 EU projects. The performances of these innovative solutions for WHR plants are examined in this work: as the working fluid is compressed in liquid phase (instead of supercritical phase like in sCO_2 cycles), the cycle efficiency can likely increase and the temperature difference in the compression step reduces drastically, allowing for a better coupling with the hot sources and reducing the stack temperature on the exhaust gases side, at constant boundary conditions, with respect to sCO_2 solutions.

In this work, for all the configurations proposed, the totality of the waste heat is recovered and partially or fully converted in electric power and useful heat in different fractions, depending on the technical solution adopted as bottom cycle. In conclusion, tanking for granted the good performances of ORC for electric-only WHR cycles [8], this work stresses the flexibility and efficient capability of CO_2-based cycles to convert waste heat into useful thermal power, while keeping satisfactory levels of electric power produced.

POTENTIAL OF WASTE HEAT IN THE INDUSTRIAL SECTOR AND THE COGENERATION BENEFITS

The EU carbon neutrality targets require an improvement of the primary energy conversion efficiency of the industrial processes to reduce their carbon footprint, and the exploitation of the available waste heat is a key strategy to meet the targets. According to a 2020 Eurostat report [9], the EU industrial sector is responsible for more than 26% of the total primary energy consumption, closely after the transport sector at 28%.

More than 70% of the energy consumption in industries is used for heating processes [10], which results in a remarkable amount of waste heat (up to 50%) dissipated in the environment [11].

Bianchi et al [12] analyzed the WHR potential in EU both in terms of technical potential (heat available from effluents and exhaust gases) and Carnot potential by considering the temperature levels of the wasted heat and converting it into mechanical power with each corresponding Carnot efficiency. It highlighted that the EU industrial sector dissipates into the environment nearly half of the primary energy consumed. According to the authors, the industrial WHR available accounts for about 920 TWh_{th}, which is 29% of the industrial consumption, while the Carnot potential is around 279 TWh_{el}.

Papapetrou [13] examined the waste heat potential in EU per sectors, temperature levels and countries, showing that one third is available at a temperature level below 200°C, 25% in the range 200–500°C and the rest above 500°C.

Moreover, power generation plants also reject large amounts of valuable heat which is currently dissipated in the environment. For instance, small scale gas turbines (5-60 MW_{el}) typically have exhaust gases in the temperature range between 450 and 560°C. Internal combustion engines (ICE) convert 30% to 40% of the primary energy into useful mechanical work, while the remaining part is released to the environment through exhaust gases and cooling systems. Exhaust gases of ICEs also have temperatures in the range 450-600 °C and they can be exploited in a WHR unit.

According to a study on the final energy demand in Europe in 2015 [14], the demand for heating and cooling (H&C) is nearly 50% of the overall final energy demand: in particular, space heating has the largest portion (53%) of the H&C demand, followed by process heating (32%).

Of the overall H&C demand, more than 20% can be located in the 100-200°C temperature range, a challenging range for any applications that has the goal of decarbonization. This fraction of heat demand is then divided in sectors, such as: pulp and paper production (230 TWh_{th}/y), food and beverage industry (123 TWh_{th}/y), the chemical (119 TWh_{th}/y) and non-metallic minerals (43 TWh_{th}/y) sectors.

Accordingly, in this work the heat recovered from the cycle heat rejection unit is differenced in heat above 100°C and below 100°C, both technically obtainable due to the high temperature difference of the working fluid across the heat rejection step, to highlight the capability of the proposed technology to also reduce the primary energy consumption of the H&C demand in the 100-200°C range and the related CO_2 emissions.

ADVANTAGES IN THE ADOPTION OF CO_2-BASED CYCLES FOR WHR APPLICATIONS

This work presents various cycle simulations where a generic waste heat source (exhaust gases) is available at a temperature higher than 420°C and can be cooled down to 125°C. The power from the exhaust gases is transferred to a heat transfer fluid (HTF) that is heated from 110°C to 420°C, used to separate the power block to the upstream process and to hypothetically adopt a thermal energy storage system. Finally, the HTF provides thermal input to the cycle, that can have a maximum temperature up to 400°C and a temperature at primary heat exchanger inlet up to 100°C, to completely exploit the available thermal power. This solution is not always optimal for only-electric configurations, where a tradeoff between the heat source exploitation and cycle thermodynamic efficiency must be considered. However, this is not the case for CHP systems where, to maximize the sum between heat and power produced, it is beneficial to completely cool down the heat source.

As detailed later in this work, ORC can efficiently be employed in WHR plant in an only-electric configuration. A graphical representation of the temperature profile of the waste heat source and a generic saturated ORC power cycle is reported in Figure 1 in a *T-s* diagram, where the nature of working fluid is not specified for generalization purposes. As evident from the figure, the heat rejection from the ORC is dominated by the isothermal condensation, rejecting heat into the ambient at temperatures lower than 45°C, a temperature level not of interest for CHP configurations. Moving from the ORC to CO_2-based mixtures used in transcritical cycles, Figure 2 depicts the power cycle behavior on a *T-s* diagram for this application. In these cases, the heat rejection from the cycle is not isothermal, and, while the fraction of heat below 60°C is still rejected by means of an air-cooled condenser, a wide fraction of this heat is at a temperature

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level valuable to be exploited in a CHP plant: the first contribution is ideally exploitable in a district heating network, while the second one can have other industrial uses, as described in the previous chapter. The fraction of heat rejected through the air-cooled condenser can be neglected if the cycle minimum temperature is sufficiently higher than 60°C: in this condition, the thermal input to the cycle is almost completely converted in the CHP plant, with the exception of a small fraction of electro-mechanical losses.

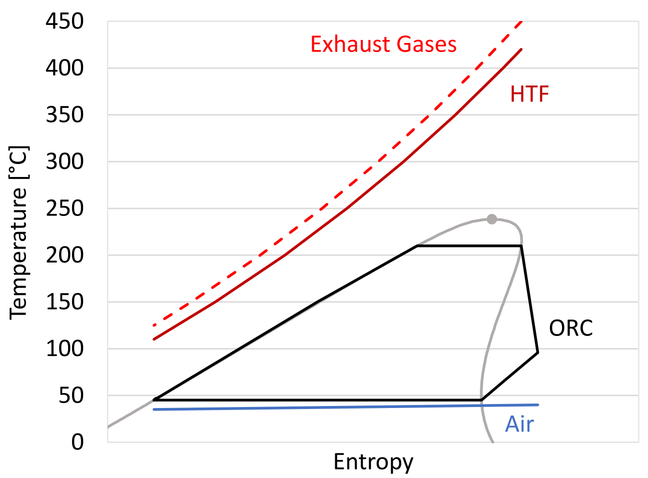

Figure 1. Temperature - Specific Entropy and heat recovery characterization of an ORC representing the state of the art of small scale WHR cycles for electricity production

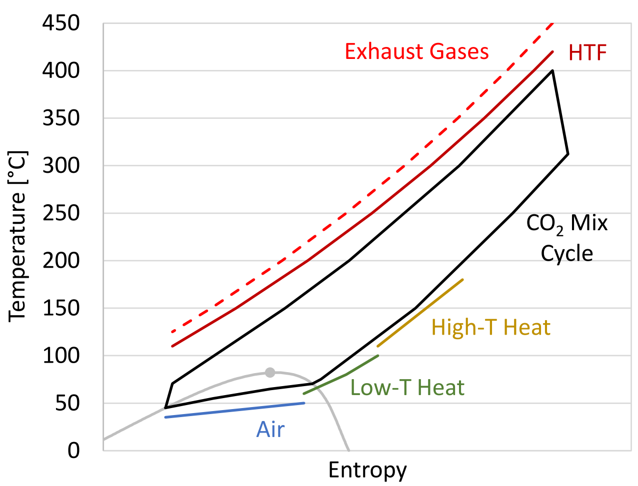

Figure 2. Temperature - Specific Entropy and heat recovery characterization of the innovative WHR transcritical cycle with a generic CO_2-based working fluid for CHP applications

While analogous considerations can be drawn also for pure sCO_2 cycles, supercritical cycles normally present lower cycle efficiency with respect to transcritical cycles especially when, as in the considered cases, the difference between the maximum and minimum cycle temperature is not considerable. In addition, the most efficient conditions for CHP applications are the ones at high cycle minimum temperature (above 60°C): in these cases the compressor power, operating far from the critical temperature of CO_2, increases non-linearly with the cycle minimum temperature and it negatively affects both the cycle efficiency and the specific work. In conclusion, underlining the concepts behind the two *T-s* diagrams proposed, Figure 3 depicts an indicative breakdown of the conversion of the thermal input performed by the two different categories of power cycles for a cycle minimum temperature above 60°C (the figures reported are indicative). As noticeable, moving from an ORC to a CO_2-based cycle solution, it is possible to better exploit the available waste heat at the expenses of a slightly lower electrical efficiency.

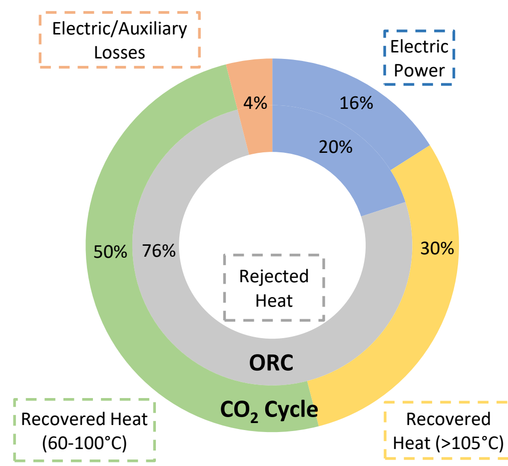

Figure 3. Indicative comparison between ORC and CO_2-based cycles in the conversion of the heat introduced in the cycle

MODELLING OF THE WORKING FLUIDS FOR THE CO2-BASED CYCLES

Two CO_2-based mixtures are reported in this work as working fluid for transcritical cycles in CHP applications, along with the performances of pure CO_2 in supercritical cycles. The first mixture is the CO_2+Acetonitrile mixture: this dopant (CAS: 75-05-8) is a flammable, non-toxic and commonly adopted fluid for many applications as solvent and in the production of chemicals. The CO_2+Acetonitrile mixture is already studied, as many VLE experimental data are available in literature, and the dopant has a thermal stability well above 400°C, suitable for this application. The mixture is modelled in ASPEN PLUS (v.11) with the standard Peng Robinson (PR) equation of state (EoS) and a binary interaction parameter (k_{ij}) of 0.055, retrieved from experimental data [15]. The second dopant considered is referred to "unnamed compound" (UC) in this work. The compound will be object of publications in the near future within the SCARABEUS and DESOLINATION framework (H2020 EU projects), and it is currently IPR protected. The dopant is considered thermally stable over 400°C, it has a low toxicity, it is not flammable and suitable for power cycles applications as it is commonly adopted as solvent for organic materials. The mixture is also modelled with the PR EoS in Aspen Plus with no binary interaction parameter, as no mixture experimental data are

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available in literature, while for the pure CO_2 the Span and Wagner EoS is adopted [16], as it is considered the gold standard thermodynamic model for pure CO_2. The CO_2+UC mixture is presented as an alternative to acetonitrile as dopant for circumstances where non-flammable fluids are of interest.

MODELLING OF THE CO_2-BASED CYCLES FOR CHP APPLICATIONS

The methodology developed to compute the nominal electric and thermal performances of the innovative CO_2 based power cycles is described in this chapter. All cycles are always optimized, in any condition, to reach the highest electric efficiency, since the heat recovery efficiency from the exhaust gases is always maximized by default, as already specified. The optimization parameters for each configuration are the cycle minimum pressure and the split ratio of the cycle splitter valve for the sCO_2 cycles; the mixture composition and the split ratio, on the other hand, for the CO_2 mixture cycles. For transcritical cycles adopting mixtures the minimum pressure is set at the bubble condition at any cycle minimum temperature.
The various CO_2-based power cycles are modelled in this work according to the assumptions listed in Table 1, assuming a unitary value of HTF mass flow rate (1 kg/s) in the ASPEN modeling tool. The quite conservative values for the cycle non idealities (mainly the turbomachinery efficiencies) are indicative of small-scale applications, in the range between 15 to 30 MW_{th}, while, at the same time, the high maximum pressures, typical of large-scale power plants for power generation, are strictly necessary for this category of power plants.

Table 1. Cycles characteristics and non-idealities

Parameter	Value
Cycle maximum temperature	400°C
Pressure at turbine inlet	250 bar
PHE/PCHE pinch point (MITA)	10°C
Compression isentropic efficiency	80%
Expansion isentropic efficiency	85%
Pressure drops (PHE / HRU)	3 bar / 1 bar
Pressure drops PCHE (HP / LP)	1 bar / 2 bar
Generator/Motor efficiency	97% / 97%
Auxiliary HRU Electric Consumption	1% of $\dot{Q}_{COND,AIR}$

Two plant layouts are adopted in this analysis: the dual recuperative layout (proposed in Figure 4) and the cascade layout (reported in Figure 5). These two layouts, which are particularly suitable for WHR applications, are modified in this work separating the heat rejection section in two different heat exchangers, one for low temperature heat and one for high temperature heat (already identified in the qualitative *T-s* diagram of Figure 2). The calculations are carried out in the simulation software ASPEN PLUS, assuming a minimum temperature difference of 5°C between the heat rejected by the cycle and the various cold sinks (the air and the two streams of pressurized water for the cogeneration uses).

In conclusion, six different cases are proposed in this work, as two plant layouts are combined with three working fluids (pure CO_2 and the two mixtures).
In addition to that, as the variability in the electric and thermal power demand is strongly case-specific for CHP plants (especially if dedicated to the industrial sector), a sensitivity analysis on the cycle minimum temperature is proposed.
As water scarcity is becoming one of the most defining global environmental problems, and water availability cannot be taken for granted in any location, water has not been adopted within this work as cold sink for the power plants. Accordingly, with only air-cooled heat rejection units, minimum cycle temperatures below 45°C are not considered. On the other hand, since the application for the low temperature heat recovered is district heating with a minimum temperature of 60°C (underlined in Figure 3), considering a pinch point of 5°C between the heat rejected and the pressurized water for the district heating would results in maximum cycle minimum temperatures of 65°C, as higher temperatures will penalize the electric efficiency with no advantages on the cogenerative section. For these reasons, the sensitivity analysis on the cycle minimum temperature is carried out in the range 45°C-65°C. When the cycle minimum temperature is lower than 65°C, the fraction of heat below this threshold is rejected in the environment with an air-cooled heat rejection unit. In this case, an electric auxiliary consumption is included to model the fan power of the heat exchanger, fixed at 1% of the rejected heat, as reported in Table 1.
Finally, as for the dual recuperative layout it is not suitable to abundantly recover heat above 105°C in conditions characterized by a low cycle minimum temperature, only the low temperature thermal user is considered at 45°C minimum temperature for this plant layout, while both the high temperature and low temperature one is modelled for higher cycle minimum temperatures.

PERFORMANCES OF THE CO_2-BASED CYCLES FOR CHP APPLICATIONS

In this chapter the main parameters to define a CHP power plant are defined and reported for the proposed solutions. The definitions of electric efficiency and thermal efficiencies considered in this work are detailed from Equation (1) to (5).

$$\eta_{el} = \frac{\dot{W}_{Turbine} \cdot \eta_{Gen} - \frac{\dot{W}_{Compression}}{\eta_{Motor}} - \dot{W}_{Aux,HRU}}{\dot{Q}_{HTF}} \quad (1)$$

$$\eta_{Th,HT} = \frac{\dot{Q}_{Rejected,HT}}{\dot{Q}_{HTF}} \quad (2)$$

$$\eta_{Th,LT} = \frac{\dot{Q}_{Rejected,LT}}{\dot{Q}_{HTF}} \quad (3)$$

$$\eta_{Th} = \eta_{Th,HT} + \eta_{Th,LT} \quad (4)$$

$$\eta_{Overall} = \eta_{el} + \eta_{Th} \quad (5)$$

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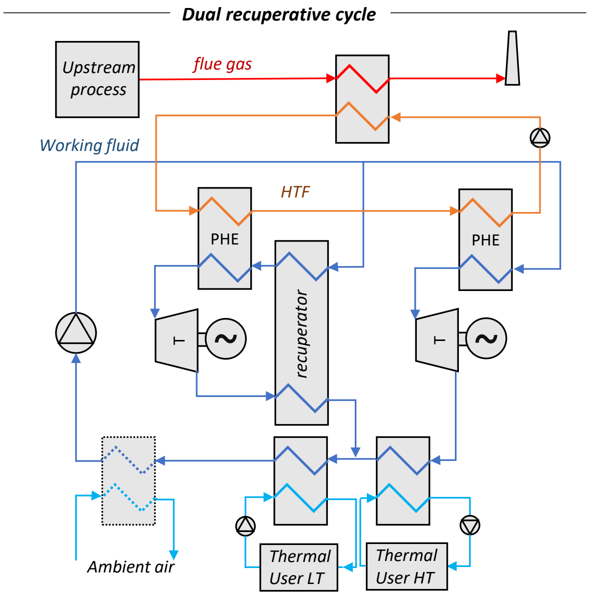

Figure 4. Dual recuperative layout for WHR power cycles.

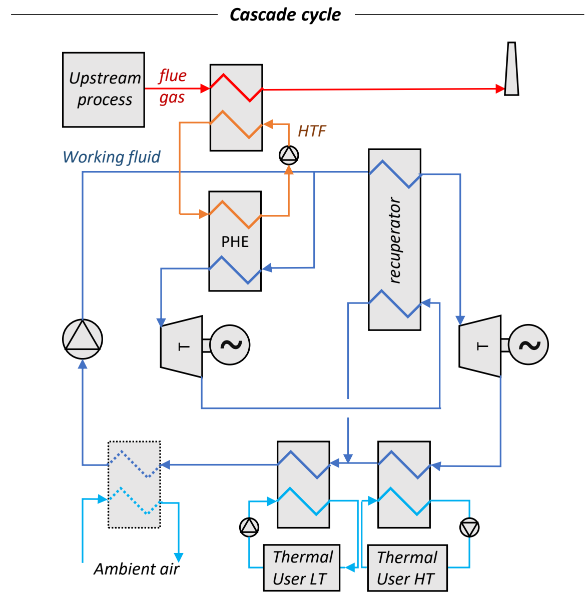

Figure 5. Cascade layout for WHR power cycles.

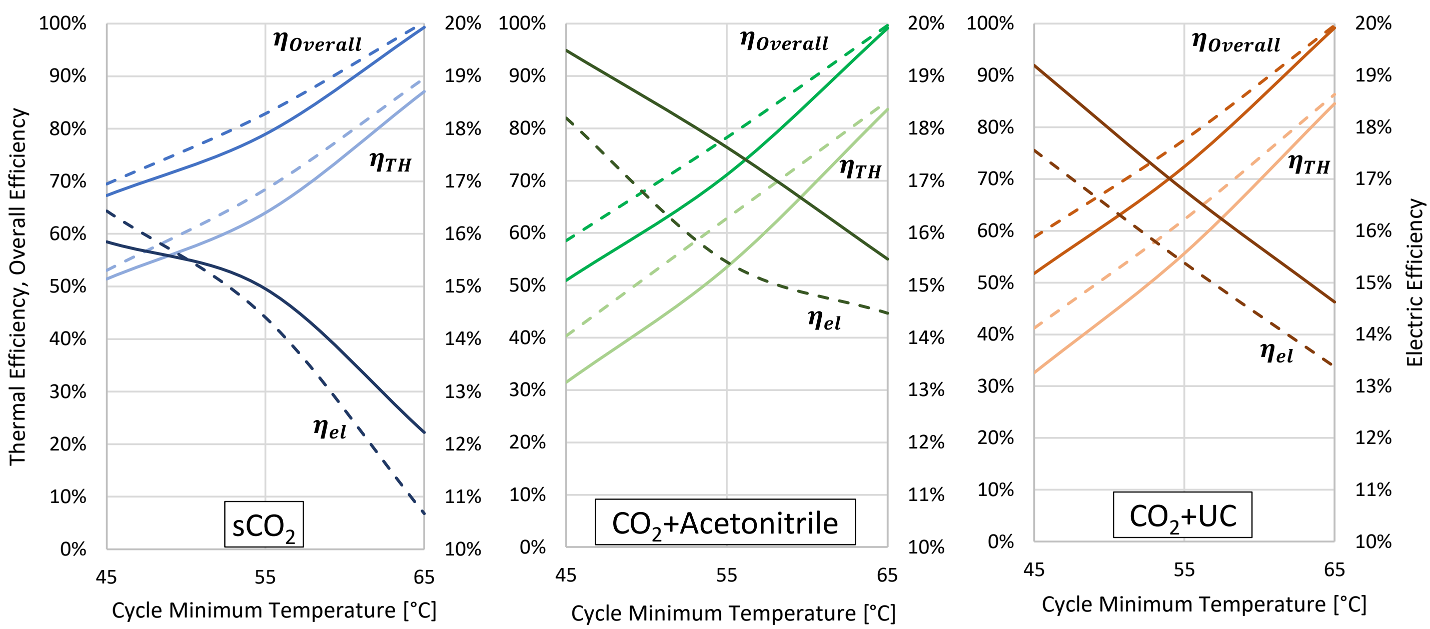

Figure 6. Trends of the electric, thermal and overall efficiency of the CO_2-based cycles adopted in CHP configuration. (Dotted line: Cascade Cycle. Solid line: Dual recuperative Cycle).

The resulting performances of the three working fluids are evidenced in Figure 6. In general, sCO_2 cycles present a more modest electric efficiency and a slightly higher thermal efficiency for the CHP applications. Especially for high cycle minimum temperatures (65°C) sCO_2 can achieve a 12.2% electric efficiency, which is 3.3% lower with respect to the mixture with acetonitrile (more than 27% lower in relative terms). The drop of electric efficiency of the proposed sCO_2 cycles is significant, in particular where the cycle minimum temperature is far from the CO_2 critical temperature. In addition, the resulting optimal molar compositions of the power cycles adopting mixtures varies with the minimum temperature. The molar composition of the CO_2+Acetonitrile mixture ranges from 94% (at T_{MIN}=45°C, 95% on a mass basis) to 89% (at T_{MIN}=65°C, 90% on a mass basis) of CO_2 content, significantly reducing the flammability risks associated to pure acetonitrile.

By contrast, the heat released from the sCO_2 cycle is slightly higher than the one from the configurations adopting the mixtures. As no thermal power is rejected into the environment when the cycle minimum temperature is set at 65°C, and no

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auxiliary consumptions of the air-cooled condenser are involved, these conditions present an overall efficiency of the CHP system ($\eta_{Overall}$) close to 100%, where only the turbomachinery electromechanical losses contribute to the power lost.
Examining the thermal power recovered in the two HRUs of the cascade cycle (taken as a reference for sake of representation), in Figure 7, it is evident that the fraction recovered at low temperature (60-100°C range) is dominant with respect to the one at high temperature (above 105°C), as defined in Equation (2) and Equation (3). For higher cycle maximum temperatures, nevertheless, the high temperature recovery efficiency can exceed 30%, becoming technically of interest for a user interested in high quality heat. The maximum temperatures of the higher quality heat vary from 170°C to 220°C, depending on the cycle minimum temperature, considering a stream at the inlet of the HT HRU unit at 105°C.
Assuming a reasonable value of thermal power from the exhaust gases for these power plant sizes (between 15 to 30 MW_{th}) the power produced from these CHP systems can be around 3-4 MW_{el} and 10-25 MW_{th}, that can be divided into 4-7 MW_{th} in the 105-200°C range and 6-16 MW_{th} for state-of-the-art district heating applications.

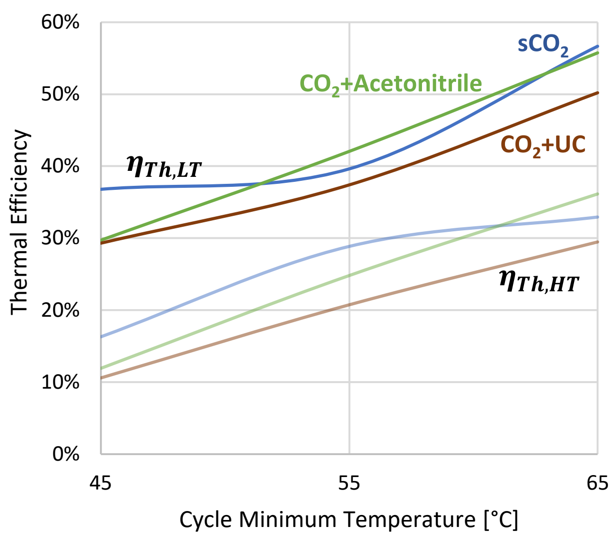

Figure 7. Thermal fraction of the thermal input recovered from the cycle HRUs for the cascade layout (Figure 5).

AVOIDED CO_2 EMISSION AND GAS CONSUMPTION OF THE CHP SYSTEMS

CHP systems are natively adopted with the advantage of reducing both primary energy consumption and carbon emissions. As a matter of fact, carbon emissions related to the thermal sector nowadays are estimated to be around 56 kg_{CO2}/GJ_{LHV} for natural gas (202 kg_{CO2}/MWh_{LHV}), while, considering the European energy mix and the share of renewable power production, for the electric sector are estimated at 74 kg_{CO2}/GJ_{el} (266 kg_{CO2}/MWh_{el}) [17]. In this work, the avoided carbon emissions are computed for the proposed CHP systems adopting CO_2-based cycles, considering as base case a condition where the electric and thermal power are produced separately with two dedicate reference plants.
Figure 8 reports the resulting avoided emissions for the cycle configurations considered in this work. The calculations are carried out assuming only 5 months per year of utilization of the thermal power for district heating purposes, considering as reference scenario a natural gas boiler with an efficiency of 90%. From the figure it is possible to notice that avoided emissions up to 30 or 35 kg_{CO2}/GJ_{th} of exhaust gases are possible with these systems. sCO_2 cycles allow for a higher share of avoided emissions for cycles minimum temperatures around 45°C, close to the CO_2 critical point, due to the higher fraction of thermal energy recovered with respect to the CO_2-mixtures power plants (around 50% higher in relative terms). On the other hand, CO_2 mixtures in cycles adopted for CHP configurations present higher avoided carbon emissions when the cycle minimum temperature is high and the overall recovery efficiency is close to 100%, as electricity covers a higher share of the overall power produced from the CHP plant with respect to sCO_2.

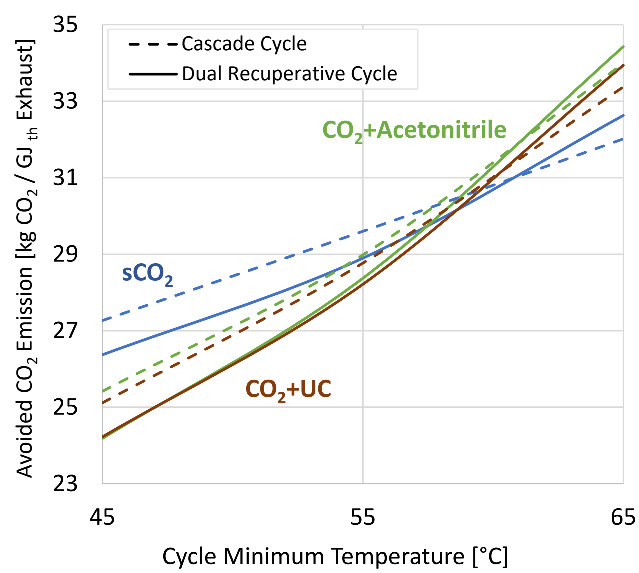

Figure 8. Avoided carbon emissions per GJ_{th} available from the exhaust gases for the various CHP solutions proposed.

Ultimately, the avoided natural gas consumption is proposed in Figure 9 since it is the main drive of the economic feasibility of any WHR power plant, both for only electricity production and for CHP applications. In practice, for each unit of thermal power released by the exhaust gases in the WHR plant, the CHP systems can avoid the consumption of 0.7 to 1.2 unit of natural gas on LHV terms. The avoided natural gas consumption is computed assuming a reference electric efficiency of 52.5% from natural gas plants (typical of a combined cycle), and the boiler efficiency previously mentioned of 90% for the thermal power generation. Coherently with the carbon emissions trends, a higher avoided fuel consumption is possible for high cycle minimum temperatures, where all heat is recovered and transformed into a useful product and no fraction is rejected in the environment with

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air-cooled heat rejection units. As for the avoided emissions, also in terms of natural gas consumption the CO_2-based mixtures show a slight edge over pure CO_2 in power cycles at high cycle minimum temperatures, in addition to provide a +3.3% electric production from the exhaust gases (more than 27% in relative terms).

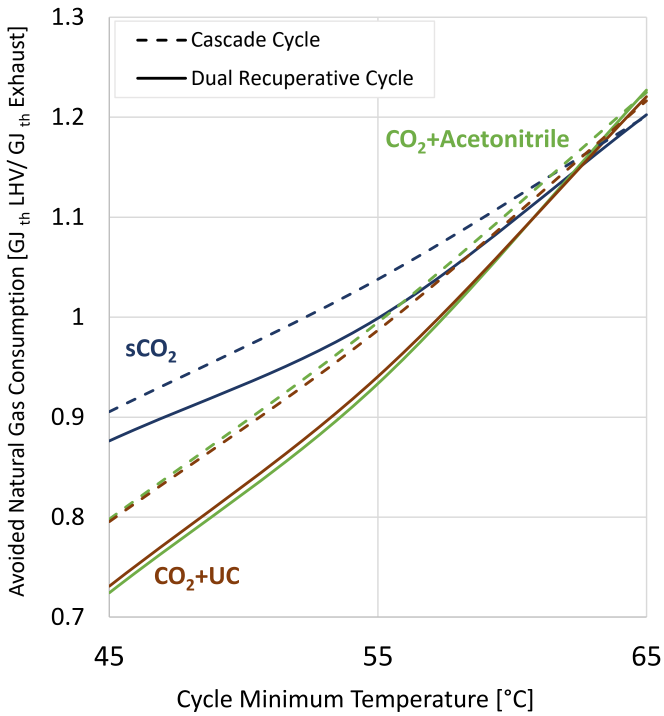

Figure 9. Avoided natural gas consumption per GJ_{th} available from the exhaust gases for the various CHP solutions proposed.

COMPARISON WITH ORC FOR ONLY-ELECTRIC WHR SYSTEMS

A comparison between the reported results of CO_2-based systems and a more conventional ORC for WHR applications is detailed in this chapter. The purpose of this comparison is to investigate the maximum obtainable electric power from the available waste heat with a category of power cycle different than CO_2-based systems and with a higher level of commercial maturity.

The electric efficiencies of Figure 6 at 45°C of cycle minimum temperature can be already considered as the maximum electric power output of the CO_2-based systems considered in this work, as all the parameters involved (cycle minimum pressure, molar compositions and mass split ratio) are already optimized to have the maximum electric efficiency for any ambient temperature, in any conditions. At the lowest cycle minimum temperature, the heat recovered in the HRUs for district heating is considered an unavoidable by-product, determined by the high temperature difference across the compression step and the non-negligible pinch point of the recuperator (PCHE), which determines a certain temperature difference that necessarily must be compensated during the heat rejection. Higher electric efficiencies are theoretically possible with the same working fluids (at constant hot source, ambient temperature and HTF temperature range) only adopting plant layouts different than the one proposed in Figure 4 and Figure 5. Nevertheless, a wider sensitivity analysis on different plant layouts is considered out of the scope in this work. For these reasons, the highest electric efficiency of the proposed CO_2-based systems for WHR applications adopting air-cooled heat rejection unit are, respectively, 16.5% for the sCO_2 cycle (cascade layout), 19.6% for the CO_2+Acetonitrile cycle (dual recuperative layout) and 19.2% for the CO_2+UC cycle (dual recuperative layout).

In contrast to CO_2-based cycles, ORC systems are investigated in this work only for electricity production from WHR plants adopting the model of Astolfi [18]: nonetheless, future works can potentially explore also ORC in CHP configurations.

Regarding the ORC plant configurations, as the vast majority of the installed ORC plants is based on subcritical cycle, it has been decided to limit the comparison to either saturated or superheated subcritical cycles adopting internal recuperator for pressurized liquid preheating from expanded vapor cooling. The optimization variables considered are the working fluid selected (among a pool of 47 candidate fluids), the evaporation temperature T_{eva}, the degree of superheating ΔT_{SH}, (equal to difference between the maximum temperature of the cycle and the evaporation temperature) and the condensation temperature T_{cond}. Coherently with CO_2 and CO_2 mixtures cases, an air-cooled condenser is considered also for ORCs, setting the minimum condensation temperature to 45°C and an auxiliary electrical consumption equal to 1% of the rejected heat. For each fluid a different upper bound on the maximum cycle temperature representative of the fluid thermal stability limit has been adopted and set equal to the maximum temperature of the experimental dataset at the base of the reduced Helmholtz energy Equation of State (EOS) provided by Refprop 9.2[19].

Adopting the same assumptions on the cycle non-idealities of Table 1 and the heat source modelling previously described, the numerical tool defines the optimal ORC operating parameters and configurations for each working fluid aiming to maximize the electric power production. Regarding condensation pressure, two cases have been considered: in case A, the lower bound is set to 1 bar in order to prevent air in-leakages due to sub-atmospheric pressures in the condenser while in CASE B this limit has been removed. Table 2 reports the results for the two cases: if minimum pressure is bounded to 1 bar the optimal cycle is cyclopentane showing for this pressure value a saturation temperature (49°C) very close to 45°C that is the lowest possible value. Lower critical temperature cycles are penalized in terms of maximum evaporation pressure that consequently limits cycle pressure ratio, while fluids having a higher critical temperature must condensate at higher temperature with a consequent performance decrease. Differently, if the minimum cycle pressure is not constrained the optimal fluid is Toluene, with a condensing temperature of 45°C and a minimum pressure of around 0.1 bar being able to reach higher evaporation

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temperatures. Both cycles are optimized in saturated condition since the inclusion of a superheating for this application is not convenient and it would result in a lower working fluid mass flow rate and a higher turbine outlet temperature that cannot be really exploited without penalizing the heat recovery from the heat source.

Table 2. Only-electric ORC solutions for WHR in this work

	CASE A	**CASE B**
Working fluid Flammabilty / Toxicity	Cyclopentane Yes / No	Toluene Yes / Yes
Electric efficiency, η_{el}	19.5%	23.9%
Maximum Pressure [bar]	40	36
Minimum Pressure [bar]	1	0.099
Evaporation temperature [°C]	229	309
Condensation temperature [°C]	49	45

Comparing these results to the ones of CO_2-based systems, no apparent improvements in cycle efficiency are evident when the ORC with cyclopentane is compared to the two CO_2 mixtures, while a +3.5% in electric efficiency is reported when adopting toluene as working fluid. However, in this case, the cycle minimum pressure results to be sub-atmospheric, leading to criticalities related to air in-leakages in the condenser (an issue not present in CO_2-based systems). It must be reminded that in ORCs it is not possible to remove the non-condensable gases by venting them in the environment using a deaerator, but instead a vacuum pump and a gas treatment unit are adopted to solve this issue, increasing the cost and complexity of operation of the plant. On the other hand, considering CHP configurations, the most favorable condition shown in this work is the transcritical CO_2+Acetonitrile cycle at 65°C minimum temperature (15.5% of electric efficiency). The drop in net electric production from the waste heat is not so drastic when moving from an only-electric configuration (ORC) to a CHP plant (CO_2+Acetonitrile), even considering toluene as adopted working fluid for the ORC. These results suggest a robust performance of the CO_2-based solutions for CHP plant in WHR applications, as, even with an abundant thermal power recovered, the electric efficiency can still compete with traditional only electric ORC solutions, at least when over-atmospheric ORCs are employed with non-toxic working fluids.

CONCLUSIONS

An innovative concept of CHP plants is presented in this paper, applied to a waste heat source of a generic industrial process. In fact, CO_2-based power cycles (both pure sCO_2 cycles and transcritical cycles working with binary CO_2 mixtures) allow for non-isothermal heat rejection from the power cycle, in any condition. Thanks to this characteristic they can be adopted efficiently both for WHR applications and in CHP configuration (by recovering the rejected heat at a temperature higher than 60°C), simply by imposing a high cycle minimum temperature.
This work underlines the beneficial aspects derived from the selection of CO_2-based working fluids for low-temperatures (< 400°C) power cycles adopted in WHR applications. It details these advantages especially when the plant location allows for a district heating network and the use of high temperature heat for additional industrial processes, both from a technical point of view and an environmental one. In fact, the recovery of a large contribution of sensible useful heat from the heat rejection unit of the cycle is the main focus of this work. These CHP systems can also be adopted in a trigenerative perspective to produce cold thermal load for residential applications, with the adoption of an absorption chiller fed by the hot thermal power normally distributed through the district heating network.
In addition, the higher electric efficiency of the WHR cycles based on CO_2-mixtures are evidenced with respect to sCO_2 cycles due to the adoption of transcritical cycles in place of supercritical ones, an effect that intensifies at low temperature difference between the hot source and cold sink of the cycle. In addition, innovative working fluids like CO_2-mixtures are proposed as an attractive technical solution for conditions where cogeneration is of interest without drastically compromising the electric efficiency of the CHP plant with respect to a more conventional solution for WHR applications, like a state-of-the-art ORC-based power system.
The mixture CO_2+Acetonitrile is highlighted as an efficient working fluid in these conditions, converting 15.5% of the waste heat in electric power and more than 80% in thermal power, both for district heating (60-100°C range) and potentially to supply high quality heat for industrial needs (105-220°C range). Future works will certainly expand the pool of possible dopants for CO_2-mixtures to be adopted in such applications, characterized by a working fluid maximum temperature in the order of 400°C.
The thermal and electric power produced by these CO_2-based power cycles in CHP configuration can potentially avoid the emission of up to 34 kg_{CO2} and the consumption of more than 1.1 $GJ_{th,LHV}$ per unitary GJ_{th} recovered from the exhaust gases, if compared to a reference scenario where the thermal and electric power are produced, separately, from conventional natural gas-based plants.

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NOMENCLATURE

List of abbreviations

CAS – Chemical Abstracts Service number
CHP – Combined Heat and Power
EoS – Equation of State
EU – European Union
H&C – Heating and Cooling
HE or HX – Heat Exchanger
HRU – Heat Rejection Unit
HT – High Temperature
HTF – Heat Transfer Fluid
HP – High Pressure
ICE – Internal Combustion Engines
MITA – Minimum Internal Temperature Approach
ORC – Organic Rankine Cycle
LHV – Lower Heating Value
LP – Low Pressure
LT – Low Temperature
PCHE – Printed Circuit Heat Exchanger
PHE – Primary Heat Exchanger
PR – Peng Robinson
sCO2 – supercritical CO_2
SH – SuperHeating
TIT – Turbine Inlet Temperature [°C]
WHR – Waste Heat Recovery
UC – Unnamed Compound
VLE – Vapor Liquid Equilibrium

List of symbols

h – Specific enthalpy [kJ/kg]
$\dot{m}$ – Mass flow rate [kg/s]
p – Pressure [bar]
Q or $\dot{Q}$ – Thermal Power [MW]
s – Specific entropy [kJ/(kg·K)]
T – Temperature [°C]
η_{el} – Electric efficiency [-]
η_{Th}– Thermal efficiency [-]

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