Waste Heat to Power: Technologies, Current Applications and Future Potential.

Erik Garofalo [a,b], Matteo Bevione [a], Luca Cecchini [a,b,1], Fabio Mattiussi [a,b,2] and Alessandro Chiolerio [a,*]

[*] *Corresponding author, e-mail address: alessandro.chiolerio@iit.it*

[a] *Istituto Italiano di Tecnologia, Center for Sustainable Future Technologies, Via Livorno 60, 10144 Torino, Italy*

[b] *Politecnico di Torino, Department of Electronics and Telecommunications, Corso Duca degli Abruzzi 24, 10129 Torino, Italy*

[1] *Now at Scuola Superiore Sant'Anna, Piazza Martiri della Libertà 33, 56127 Pisa, Italy*

[2] *Now at SPEA S.p.A., Via Torino 16, 10088 Volpiano (TO), Italy*

Abstract

Energy consumption, environmental impact and sustainability fastly rose through the rank, achieving the first places in driving investments, policies and concerns of all Countries at any developmental stage. Energy transformation, though, must cope with non-unitary efficiency of devices and processes, which results in a distributed production of waste heat. A reduction of emissions, implying a conversion of waste heat to more noble forms of energy and a concurrent increase of efficiency of the same devices and processes, is of paramount importance. In view of the enthalpy content and distribution of the different sources of waste heat, low grade/low enthalpy sources below 200 °C are considered the most fertile field for research and development, with an impressive industrial growth rate. Thermodynamic cycles and thermal conversion devices based on the most relevant physical effects are here introduced and briefly described, including both solutions that already achieved industrial maturity, and less developed systems and devices whose study is still in progress. A specific focus on three application domains, selected in reason of their economic relevance, is done: industrial processes for the vast energy and capital availability, automotive sector for its permeation, and wearable devices for the market size. Limits and opportunities are critically

discussed.

Nomenclature

- Barium Titanate (BT)
- Barrel of Oil Equivalent (BOE)
- Brayton Cycle (BC)
- Carbon Dioxide Trans-Critical Cycle (CDTCC)
- Carbon NanoTubes (CNT)
- Electric Turbo-Compounding (ETC)
- Exhaust ThermoElectric Generator (ETEG)
- Figure of Merit (FoM)
- Gas Turbine (GT)
- GreenHouse Gase (GHG)
- Heavy-Duty Vehicle (HDV)
- High Temperature (HT)
- Industrial Wireless Sensor Network (IWSN)
- Internal Combustion Engines (ICE)
- International Energy Agency (IEA)
- Kalina Cycle (KC)
- Lead zirconate titanate (PZT)
- Life Cycle Assessment (LCA)
- Light-Duty Vehicle (LDV)

- Liquefied Natural Gas (LNG)
- Liquefied Petroleum Gas (LPG)
- Lithium-Ion Battery (LIB)
- Low Temperature (LT)
- Magneto-Caloric Effect (MCE)
- Mechanical Turbo-Compounding (MTC)
- Medium Temperature (MT)
- Organic Rankine Cycle (ORC)
- Poly (3,4-EthyleneDiOxyThiophene) TolueneSulfonyl (PEDOT-ToS)
- Poly VinyliDene Fluoride (PVDF)
- PolyEthylene Naphtalate (PEN)
- PolyStyreneSulphonate (PSS)
- PolyVinyl Chloride (PVC)
- Power Conditioning Unit (PCU)
- PyroElectric (PE)
- PyroElectric Generator (PEG)
- Rankine Cycle (RC)
- Return On Investment (ROI)
- Solid Oxide Fuel Cell (SOFC)
- Steam Rankine Cycle (SRC)

- Stirling Cycle (SC)
- Stirling Engine (SE)
- Supercritical CO_2 (SCO_2)
- SuperCritical Rankine Cycle (SCRC)
- TetraThiaFulvene-TetraCyaNoQuinodimethane (TTF-TCNQ)
- ThermoElectric (TE)
- ThermoElectric Generator (TEG)
- Trilateral Flash Cycle (TFC)
- Ultra-Low Power (ULP)
- Waste Heat Recovery (WHR)
- Waste Heat to Power (WHP)
- Wearable ThermoElectric Generator (WTEG)

1 Introduction.

1.1 An ecological overview.

Energy-related issues, including the location and exploitation of resources, the costs of extraction, transformation and distribution, accessibility and demand, as well as awareness about use and consumption, are of paramount importance at this moment in time. The governments of every developed nation are allocating increasingly wider funding to evaluate problems such as those listed above. Three key examples of this are: 1) the International Energy Outlook 2019 delivered by the US Energy Information Administration, 2) the independent assessment issued by the UK Committee on Climate Change by request of UK Government, and 3) the European Green Deal for a climate neutral EU within 2050, with a plan to invest 1 trillion EUR. As regards the UK, the national target defined by the Government is the achievement of more than a 20 % increase in industrial energy efficiency by 2030. Action plans are therefore required by virtuous Governments, to support innovation and make it easier to access financial resources[1]. As an example, the world′s largest fund manager, BlackRock (close to 2.64 trillion EUR) announced to the U.S. Securities and Exchange Commission the launch of a money-market fund primarily investing in developed environmental practices[2].

According to a study conducted by Vaclav Smil[3], the world energy consumption has followed a monotonically increasing trend since the beginning of the first industrial era (1840). As can be noticed in Fig. 1, the speed of this growth has recently increased.* Energy consumption is an excellent indicator for the maturity level of economics, in particular growth/recession. In the first period of industrialization, energy consumption experienced a constantly increasing superlinear trend. At a global scale, when the period of post-industrialization began, economic growth started to stabilize and ultimately decrease, and the associated energy consumption followed a fairly similar trend. CO_2 emissions are also directly correlated with economic growth.[4] Energy is the fundamental source transformed by our everyday life processes, spanning from the

* Data source: Global Energy Statistical Yearbook website, the most recent available (2018).

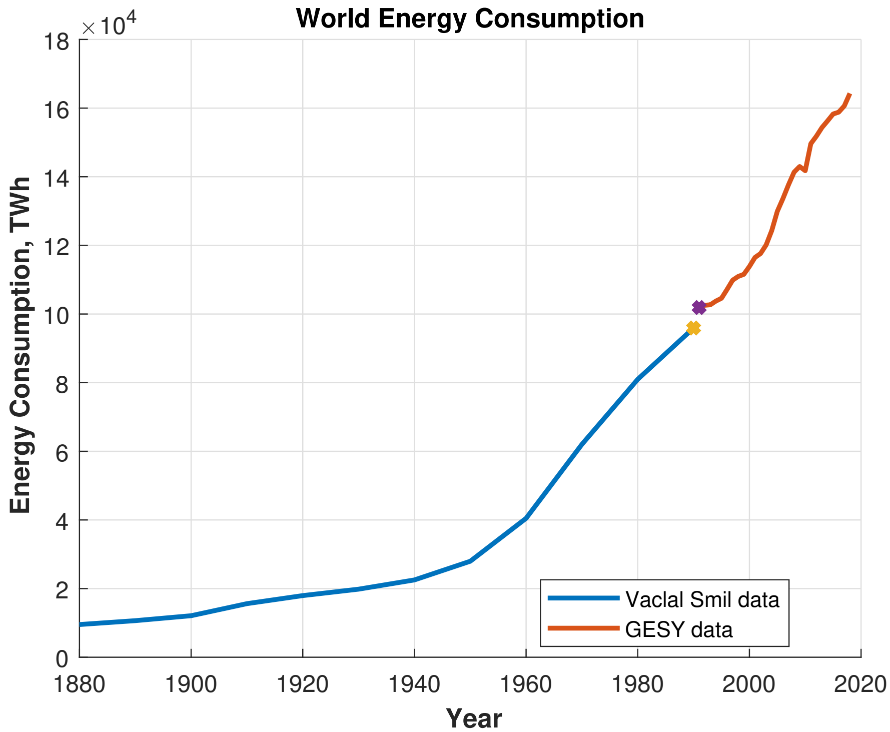


Fig. 1 Global energy consumption trend during the last 140 years. The energy sources that have been taken into account are: coal, crude oil, natural gas, hydroelectricity, nuclear electricity and biofuels for data until 1990. The data provided by the Global Energy Statistical Yearbook (red) are more precise and complete, for this reason the two curves are slightly mismatched at 1990 entry.

residential, to mobility, to the industrial sectors, including food as the basic source of our physiological activity. Due to global warming, increasing energy costs and green politics, the search for sustainable, responsible, clean resources represents a highly impacting and exponentially growing sector. According to a review of energy consumption at the global level, it is evident that most of our energy is derived from fossil fuels, while renewables account for less than a quarter of global consumption worldwide. [5]

The over-exploitation of energy sources may result in criticalities, at the political, social and logistic level. It is therefore of fundamental importance to increase energy efficiency at the scavenging/harvesting/transformation level. [4] Regarding the operation of industrial and power plants, dilemmas arise about how to increase efficiency, how to better convert energy between its forms, and how to utilize waste heat arising from thermodynamic inefficiencies (for example due to friction, thermal dispersion, electromagnetic induction, etc.) or practical needs. The creation of a common approach with a new attitude towards our fragile natural environment is required. Alongside an increase in the consumption of primary energy, the amount of waste heat increases, therefore representing a greater economic and ecological potential for utilization. Although waste heat may be exploited, ideally it should be avoided: this is done through the energy optimization of processes by needs-based controls, process operation and design, improved insulation, the use of highly efficient electric drive systems and a change towards more energy efficient production methods. However, even after energy optimization, significant potential remains.[6] Enormous amounts of waste heat injected into the environment also have the side effect of locally increasing the atmospheric temperature, especially in urban environments, slightly moving solution equilibria of several gaseous species. Focusing on the main GreenHouse Gases (GHG) and listing them in order of importance, according to the Intergovernmental Panel on Climate Change (IPCC)[7] [8], they are:

- **Water Vapour** is the major contributor of all since it provokes from 30 to 70% of the overall greenhouse effect[9] [10]. The reason for its potential resides in the large amount of this chemical species in the atmosphere, enabling a positive feedback loop;

- **Carbon Dioxide** is the principal gas monitored because, even if it absorbs less heat per molecule than others, it is more abundant and has a longer lifetime in air (thousands of years with respect to the decades of methane). Furthermore, it plays an important role in regulating the pH of the oceans, since these represent the main CO_2 reserve, and its increase provokes acidification. Another positive feedback effect can be found here: a temperature increase leads the oceans to release CO_2 into the atmosphere because of the decrease in solubility;

- **Methane**: the impact of this gas on the greenhouse effect is 60 times that of CO_2 and a monotonic increase in the last decades has been registered. However, its level and lifetime are low enough to keep its contribution under control;

- **Nitrous Oxide**: its capability to absorb heat is 300 times that of CO_2 and around 40% of total N_2O emissions are caused by human activity. Moreover, its lifetime in atmosphere is over 110 years making it one of the most persistent GHG;

- **Ozone** is naturally present in the upper level of the atmosphere and, in contrast with the previously analyzed gases, mainly absorbs the radiations coming from the Sun instead of those reflected by the Earth's surface.

To estimate the amount of waste heat Q [J] released, for example, from a continuous hot vapour volume into the environment, it is possible to use Equation 1:

$$Q = c\,m\,\Delta T \tag{1}$$

where m [kg] is the mass of the hot vapor volume, c [J kg^{-1} K^{-1}] the heat capacity of the vapor and ΔT [K] the temperature difference between the hot vapor and the ambient environment. Additionally, the heat coming from phase transformations (latent heat) must be taken into account, which is released after the condensation of a gas or the solidification of a liquid. Thus, the higher the mass flow and the ΔT between hot and cold reservoirs, the greater the waste heat amount. To understand the abundance of this source, its economic value and the importance of converting it into more noble energy forms as proposed by Waste Heat to Power (WHP) applications, the average efficiency of industrial processes and thermal machines should be considered: between 30 to 60 % of the overall energy consumed is wasted into the environment as heat. Other fundamental aspects also play a role and must be considered in a multi-variable optimization model, before any technology is adopted:

- **Time availability**: the temporal distribution of energy availability throughout a day, week and season, where a more continuous flow is always preferred; to increase heat stability in time, heat storage could be implemented, which is another huge field under development;

- **Thermo-economic analysis**: this aspect takes into account the Return on Investment (ROI), usually comprising between 5 and 10 years, to pay back the installation;

- **Environmental sustainability** should also be evaluated through a full Life Cycle Assessment (LCA) of plant / device life expectancy, development costs and decommissioning.

It is almost impossible to find studies addressing all the three fundamental aspects evidenced above, with rare exceptions[11]. To give a greater breadth to the thermodynamic analysis, in particular dealing with heat, a form of energy that intrinsically contains entropic (dispersive) terms, it is worth recalling the concept of exergy, by definition: *the total amount of energy that can be extracted from a physical system given its position in an external environment*. The concept of exergy brings together two aspects of an energy transformation process: its *quality* and its *quantity*. Ideal thermodynamics is conceived as a far-from-reality analysis, where processes are deconstructed as an integral of infinite processes in quasi-equilibrium. Exergy analysis is fundamental for Waste Heat Recovery (WHR) processes, as its outcomes take into account the sources of irreversibility which are intrinsic to real processes[12] [13].

1.2 WHP economic potential.

As can be noticed, taking into consideration the total amount of waste heat generated: the 72% of global energy consumption is lost in form of heat[14], totalling 12 PWh/year. The 66% of this heat is available at Low Temperature (LT) conditions below 200 °C, which is the focus of our review paper, totalling a bit less than 8 PWh/year; 25% is available at medium temperature (MT), between 200 and 500 °C, totalling 3 PWh/year; the last 1 PWh/year is available at high temperature (HT), with conditions above 500 °C. The average heat to power efficiency for conversion in the two temperature/entalpy ranges covered by this review are: 15% (LT) and 45% (MT) as highlighted in section 7. Therefore, excluding HT from the analysis, a possible amount of noble (i.e. electric) energy recovered from waste heat and injected into the grid or used locally is estimated to be around 2.5 PWh/year, generating a turnover of more than 300 billion EUR if the electricity is sold to industries (@ 0.125 EUR/kWh which is the 2015 cost towards industrial consumption) or more than 550 billion EUR if sold to households (@ 0.221 EUR/kWh which is the 2015 cost towards households consumption).[15–17] A bulk of 2.5 PWh/year represents 1.5%

of the global energy production. However, the cost per kWh generated could be much higher, considering the installation costs for WHR/WHP solutions, and must benefit from intelligent politics aimed at sustaining research, development and production of highly efficient integrated processes and investment in equipment manufacturing. On the other side, a more economical way of recovering waste heat is through direct use of the heat as it is.[18] According to market reports estimates for the WHP market size, a significant value of 13.2 billion EUR has been pointed out for 2018 and, expecting a Current Annual Growth Rate (CAGR) of 13 %, its valued in 2025 will approach 26.4 billion EUR.[19]

1.3 Review outline.

The following sections provide a complete review of technologies available at present day to recover thermal waste and convert it to more noble forms of energy. The outline is as follows: in section 2 thermodynamic cycles and thermoelectric devices that have already achieved industrial maturity are described; in section 3 thermodynamic cycles and conversion devices based on less known physical effects that have shown profitability and are currently available at research or pilot scale are described; in section 4 a specific focus on the most relevant application domain for capital intensity, that of industrial production plants, is given, followed by section 5 presenting a focus on automotive sector for its permeation and intermediate characteristics of portability and complexity, and finally by section 6 for the potential market size of portable waste heat to power applications. The last section 7 provides a final comparison between technologies and anticipates, in our critical vision, future developments in the field.

2 Current technologies

In this work, a large number of WHR methods have been described: they are divided into thermodynamic approaches on one side and cross-thermal effects on the other one. Examples of the first category are: the Brayton Cycle (BC), first introduced and quite common in airplanes and gas power plants for its marginal maintenance costs; the Stirling Cycle (SC), operating homonymous engines, which feature good efficiency, lower pollution, silent operation, and are simply configured, reliable, with multi-fuel capability; the Organic Rankine Cycle (ORC); the Kalina Cycle (KC); the Carbon Dioxide Trans-Critical Cycle (CDTCC). On the other hand, examples of the second category are: ThermoElectric (TE) devices; PyroElectric (PE) devices. At the nanoscale, mixed effects are typically enhanced thanks to both thermal and other physical properties (i.e. electronic, magnetic, etc.), enabling the direct conversion of temperature gradient. Although this flied is still mainly unexplored, it is very promising.[20]

2.1 Thermodynamic machines

2.1.1 Brayton Cycle

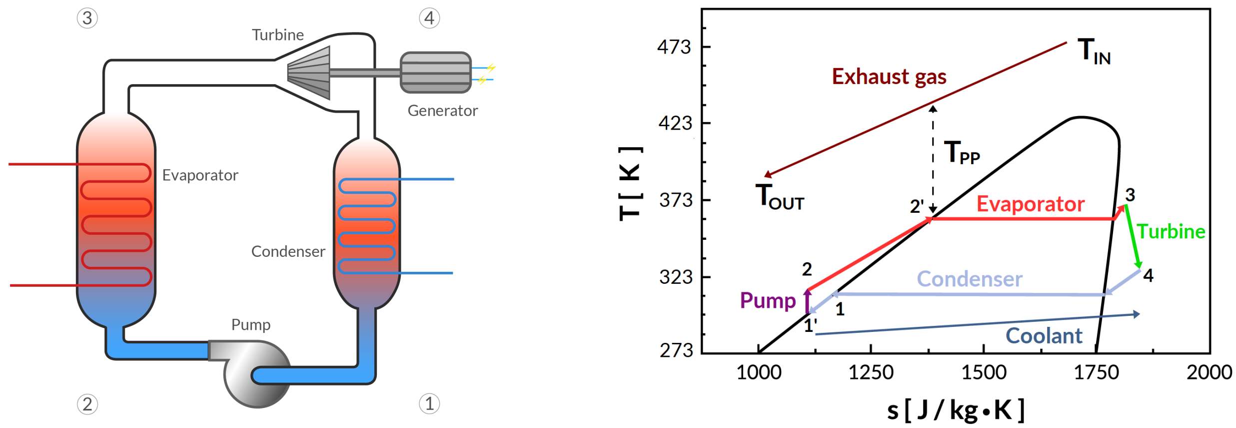
The BC is characterized by a process in which air is compressed isentropically by a compressor, then it receives heat from exhaust gases at constant pressure and finally it expands isentropically in a turbine to generate electrical power. At this point, the air is discharged back to atmosphere and the process is repeated. BC represents an optimal choice for WHR systems working at mild temperatures in the industrial sector. This approach has been explored in the 1980s to convert waste heat from adiabatic engines, enabling a reduction of running costs on one side and a reasonable additional capital investment on the other. Recently, Zhang *et al.* (2015), proposed a BC WHR system for the blast furnace slag in iron and steel industry.[21] Song *et al.* (2013) integrated a BC WHR system into a Diesel engine, connecting the turbocharger compressor with the compressor that operates on the BC. Results showed that the fuel economy of the Diesel engine can be improved by 2.6 % at fast rotation regimes and 4.6 % at lower regimes, under full load.[22] Galindo *et al.* (2015) investigated WHR for internal combustion engine exhaust gases using a BC machine.[23] Gequn *et al.* (2015) proposed a CO_2 based BC to recover the engine exhaust heat and compared its performances with an air-based BC. If compared to a BC based on air, the results have shown that CO_2 cycle provides better results, including net output power, thermal efficiency and recovery efficiency.[24]

2.1.2 Stirling Cycle

In the SC the gas medium (usually air, helium or hydrogen) is compressed isothermally. It follows a passage through a regenerator (or heat exchanger) that operates at constant volume, where an amount of heat is absorbed by the gas, which raises its pressure and temperature. Then the gas is submitted to an isothermal expansion and finally the hot gas goes back through the regenerator, releasing an amount of heat. The Stirling Engine (SE) has several features that make interesting its application, especially in conjunction with Gas Turbine (GT) cycles where waste heath is generated: it is silent and its working fluid can operate without any mixed phase operation. Furthermore, it is simple to power-up and is sealed only towards the cold section.[25] Quite recently the combined operation of GT and SE has been studied from a thermodynamic point of view. Hou *et al.* (2018) introduced a double action thermoacoustic SE-based electrical generator capable of recovering Liquified Natural Gas (LNG) cold exergy, converting the external thermal energy into acoustic work (the operating temperature is between LNG and ambient temperature).[26]

2.1.3 Organic Rankine Cycle

Based on Rankine Cycle (RC), ORC are steam-like systems that use organic working fluids instead of water, allowing to harvest waste heat at temperatures up to 300 °C.[27] In ORC machines hydrocarbons, siloxanes, refrigerants and CO_2, can be exploited instead of water, thanks to their advantageous properties in low temperature applications: lower boiling and critical points, lower specific volumes, as well as lower viscosities, higher vapour pressures, and higher molecular masses with respect to water-based fluids.[27] Furthermore, ORCs are very much appreciated in current research for the availability and the simplicity of their components and for



(a) ORC schematic **(b)** Example of ORC TS diagram.

Fig. 2 Fig. 2a represents a typical schematic of an ORC system where all the components and thermodynamic transformations are shown. Fig. 2b represents an example of TS diagram using R245fa as organic working fluid.

the low flammability, corrosion and toxicity of working fluids. Nowadays, several ORC-based plants are installed in different countries (Italy, Austria, Germany, the Netherlands, Sweden, U.S.A., Canada, etc.) and the number of plants is still growing. The adaptability and the scalability of this technology permit to generate power from different heat sources (from industrial to domestic applications), selecting the dimension of the components and matching them with the choice of the working fluid. In recent years, this technology has been widely employed also in the transportation sector.[27] The working principle of ORC is shown in Fig. 2a and its temperature-entropy (TS) diagram in Fig. 2b: a pump pressurizes the working fluid in liquid form (from point 1 to point 2); heat is then moved from the heat source to the refrigerant (working fluid) through a super-heater and an evaporator, where the organic fluid gets vaporized (from point 2 to point 3); then, the high pressure working fluid flows into an expansion turbine, connected to the load (electrical power generator) (from point 3 to point 4); at the end, the cooling source controls the organic fluid returning back into liquid form in the condenser (from point 4 to point 1). There are many factors that can affect the ORCs' performances. In case the available energy is small and the available source is low-grade, to safeguard the overall performance of ORCs, attention is given to expanders (centrifugal or axial-flow turbines, allowing the expansion of the high-pressure gas) since they play a key role.[1] Bademlioglu et al. (2018) provide a statistical analysis on system efficiency, using the Taguchi method.[28] In an ORC system, the main parameters affecting the design are: choice of the working fluid, pinch point, superheating temperature, evaporator and condenser temperature, heat exchanger effectiveness, pump and turbine efficiency, installation and running costs.

2.1.4 Kalina Cycle

The KC is an absorption-based power generation cycle, based on RC. The working fluid enabling KC systems is a mixture of ammonia and water, in order to increase the recovery efficiency. Condensed water-ammonia mixture is compressed isentropically, then it is heated at constant pressure while it evaporates (first the ammonia, then the water), subsequently it is isentropically expanded into a turbine, and finally condensed (first the water and then the ammonia) at constant pressure releasing heat. The operating temperature lies between and 90 and 500 °C. With respect to ORC and supercritical cycles, KC shows superior performances. Since the temperature difference between the working fluid and the heat source is reduced, reversibility is increased and dissipation limited. With respect to RC, where a considerable amount of heat is lost during the isothermal vaporization of water to steam, the binary mixture in the Kalina cycle vaporizes non-isothermally, improving the efficiency of the cycle.[29] Moreover, KC has one more degree of freedom compared to RC, since it is possible to act on: the NH_3:H_2O ratio in the working fluid and the system pressure levels. In fact, using a mixture as working fluid permits to manipulate the pressure in the system by varying the composition. In this way, the thermal performances are maximized.[30] At given cooling conditions the pressure in the condenser can be reduced by diminishing the ammonia concentration. Increasing the ammonia concentration may raise the evaporation pressure.[29] While KC allows a higher thermodynamic efficiency, the split ammonia and water streams add complexity and may require an additional pumping system. For this reason, plant operators and developers have different opinions about the potential of KC to overcome Rankine-type power plant performance.[31] Another relevant feature of NH_3:H_2O mixtures is the extremely low amount of oxygen dissolved in the fluid, that severely reduces oxidation likelihood and running costs.[1] This process allows for flexibility in choosing boiling points which can compensate for temperature fluctuations in the heat flow. Nevertheless, it is a technically complex system so it is much more capital intensive and far less tested than ORC modules. In the same range of temperatures it comes out that ORCs are 15 – 25 % less efficient than KCs, with the tangible outcome that power plants featuring hot fluid below 150 °C are increasingly based on this new technology.[27] Several specific applications have produced adaptations of KC systems, with more than 30 solutions which have been introduced so far. For example, in cement industry, superheated NH_3:H_2O vapor is generated harvesting low-grade heat; it is then expanded in a turbine, condensed in regenerative heat exchangers, diluted and fed into a low-pressure condenser, and finally injected into the high-pressure condenser before reaching again the vapor generators.[1]

2.1.5 Carbon Dioxide Trans-Critical Cycle

As above mentioned, to recover or convert waste heat by means of thermal machines, organic and natural fluids are often used. Worth noting, CDTCC technology, being based on CO_2, provides non-toxic, non-flammable, non-corrosive operation. CO_2 reaches the supercritical state at 7.38 MPa and 31.1 °C and is therefore widely applied to low-grade heat recovery systems.[32] By intelligent design of a CDTCC system, heat is rejected below the critical point and absorbed above, having therefore a working fluid in the superheated state under supercritical pressures, resulting in maximized performances.[33] The working principle is the same described in the ORC, but in this case, CO_2 is isentropically compressed, heated at constant pressure, isentropically expanded and finally condensed releasing heat at constant pressure. Cayer *et al.* (2009) applied four different methodologies on a CDTCC power cycle with a low-grade energy heat source and performed a parametric optimization.[34] Li *et al.* (2017) theoretically compared a CDTCC power cycle and a R245fa ORC, operating on a low-grade heat reservoir and concluded that the exergy efficiency would benefit from using a recuperator.[32,35]

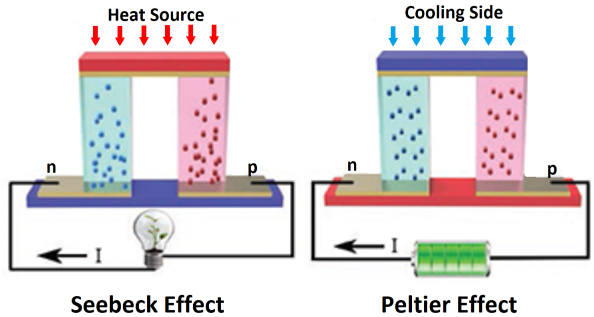
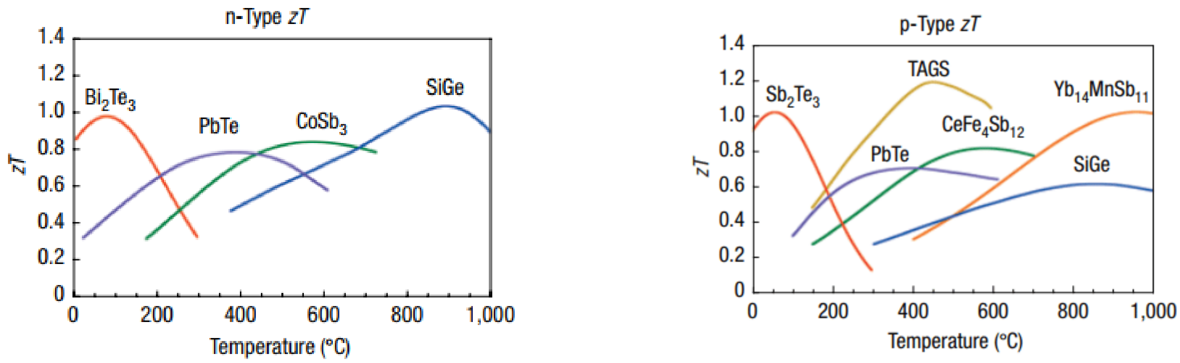


Fig. 3 Thermoelectric effects: in the left figure the typical representation of a thermocouple based on Seebeck effect is reported whereas in the right one, the Peltier effect is represented.

2.2 Thermoelectric systems

TE devices also belong to WHP/WHR technologies, but have rather different features with respect to thermodynamic cycles. First of all TE systems are solid state devices, which transform heat into electricity by means of Seebeck effect in several application domains such as factories, power plants, computers, vehicles, stoves, and wearable devices with a compact design.[27] The Seebeck effect derives from the capability of a material to produce a current when submitted to a temperature gradient. The tendency of a material to manifest this effect is represented by the Seebeck Coefficient S [V K^{-1}] which is a non-linear function of the temperature and it is specific for each different material and crystalline configuration. In Fig. 3 the typical apparatus of a thermocouple (the first device exploiting the Seebeck effect) is shown. TE materials are currently commercialized for integration into high performance cooling systems needed to realize high heat-fluxes to very low temperatures at precise rates.[27]

In general, the materials can be divided in three categories depending on the temperature of operation: low (below 250 °C), medium (250-600 °C) and high (above 600 °C) working temperature. Since the first devices until nowadays, Bismuth is the most widely used material for low-temperature applications. The Seebeck coefficients is deeply dependet on the effective mass and mobility of the carriers[36]. For this reason, antimony-telluride Sb_2Te_3 or its alloys are used for p-type composition instead of bismuth-telluride, since their higher carrier mobility. One important property of these alloys is the possibility to adjust the carrier concentration and,



(a) n-type material FoM vs temperature **(b)** p-type material FoM vs temperature

Fig. 4 The material FoM of different n and p type material are plotted with respect to the temperature in fig (a) and (b), respectively. For the low-grade waste heat to power, thus T$\leq$ 200 ℃ ,Bi_2Te_3 and Sb_2Te_3 show the highest zT value. Reproduced with permission.[36] Copyright 2008, Springer Nature.

hence, finely tune the material specific Figure of Merit (FoM)†. Moreover, Fig. 4 shows why both Bi_2Te_3 and Sb_2Te_3 are, at LT, the most suitable materials to be used, since they feature the highest FoM in this temperature range.

Recent studies by Pacific Northwest National Laboratory considered some well known industrial activities, such as aluminum smelting, glass manufacturing, and cement production, and concluded that small internal combustion engines could be profitably replaced by external combustion TE engines, vibration-free and less impacting from the acoustics point of view. TE engines can be driven using several fuels, as for example propane, butane, liquefied natural gas, bio-alcohols, and not necessarily based on fossil sources.[37] Both United States and Japan Governments have introduced regulations to help companies introducing TE devices in trucks and cars to partially convert waste heat from the exhausts into electricity, powering steering, brakes, water pumps, turbo-chargers, etc. Although efficiency estimates depend on the degree of system integration and on driving conditions, Diesel consumption (nowadays highly diffused among developed countries to enable on site power generation) could be reduced by 5 to 10 %[37]. Several leading automotive manufactures such as Volvo, Volkswagen, BMW, and Ford are introducing WHR systems able to provide around 1 kW of electrical power and increase consequently the

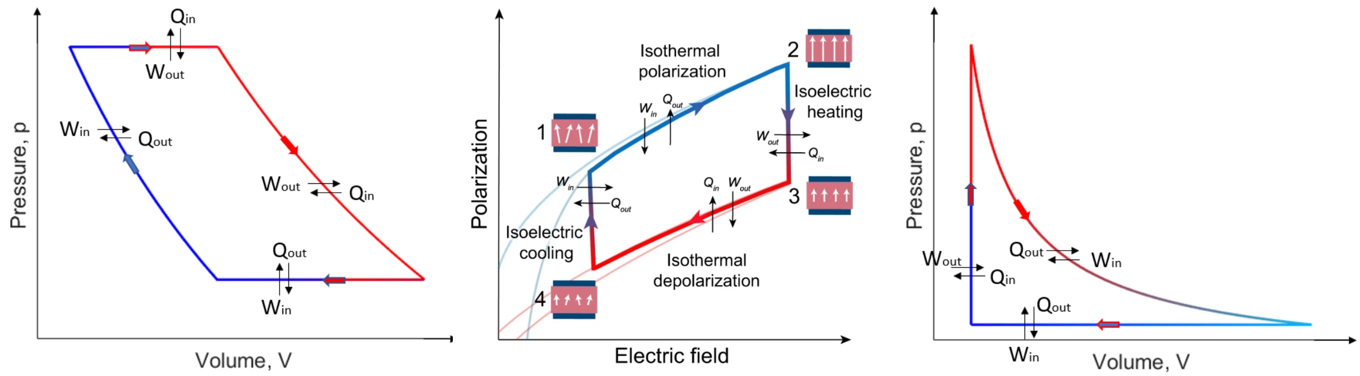
† The term figure of merit is referred to a parameter or a physical quantity used to characterize the material performances with respect to other alternative elements.

thermal engine overall efficiency by using TE generators. Hsu *et al.* invented a WHR system for automotive exhaust heat recovery composed by 24 TE modules able to provide approximately 12 W (electrical) with a ΔT of 30 °C [27]. Sano *et al.* developed a very efficient TE module (15 % efficiency) [27]. Furthermore, Solar Thermoelectric Generators (STEGs) have been developed efficiently coupling thermal solar collectors with TE devices, since the absorbed heat is conveyed on the TE devices by means of a diathermal fluid.

2.3 Pyroelectric systems

Another effect that can be exploited in energy harvesting, is pyroelectricity, through the so called pyroelectric (PE) effect. Unlike thermoelectricity, where a stable (stationary) temperature gradient is needed, this effect allows to displace electrical charges from temporal temperature changes across a suitable material or device. PE allows to avoid the main issue of Thermoelectric Generators (TEGs), i.e. the need of huge heat flows in order to sustain a large temperature gradient. This observation has brought attention on PE devices which promise a better efficiency and ease in installation. The main parameter defining the PE performances is the pyroelectric coefficient [C $m^{-2}K^{-1}$], described as the change in the spontaneous polarization vector with respect to temperature. Several kinds of PE materials have been studied trying to find the best compromise to enhance efficiency in the realization of PE generators (PEGs). Lead zirconate titanate (Pb,Zr)TiO_3 (PZT) or barium titanate $BaTiO_3$ (BT), feature the highest known PE coefficients (-268 and -200 $\mu C\,m^{-2}\,K^{-1}$, respectively). A collection of information about the most popular PE materials has recently been produced [38]. In the work developed by Sebald *et al.* (2009) a comparison between the performances of TEGs and a PEG is reported [39]. It is shown that linear materials, i.e. those having the dielectric constant which increases linearly with the applied electric field, are able to produce just few μW cm^{-3} for temperature variations of 20 °C with a frequency of 10^{-2} Hz. However, using nonlinear materials, the performance can be strongly increased by adopting particular thermodynamic path cycles like:

- **Ericsson** cycle, consisting of two isobaric transitions, isoelectric in the polarization-E plane, [41]



(a) Ericsson cycle **(b)** Olsen cycle **(c)** Lenoir cycle

Fig. 5 The 5a represents the typical trend of an Ericsson cycle. The 5b image is representing the typical Olsen cycle where the polarization is represented as a function of electric field E.[40]. Finally, the graph 5c represents the Lenoir cycle. The colourmap indicates the temperature variation.

and two isothermal transitions, a compression and an expansion.[42] It is represented in Fig. 5a;

- **Olsen** cycle, formed by two isoelectric processes and two isothermal ones. Several experiments have been conducted with different materials under different crystalline forms (e.g. single crystal and thin film).[43–45] It is represented in Fig. 5b;

- **Lenoir** cycle, It is a formed by 3 transitions: isochoric heat injection, isoentropic expansion and isobaric heat rejection. Mohammadi *et al.* (2012) showed that this cycle in comparison to the Ericsson one results in a much bigger amount of harvested energy in the latter.[46] It is represented in Fig. 5c.

In the work of Sebald *et al.* (2009) the results obtained testing different materials are reported, and the increase of power output is quite evident, moving from a few μW cm^{-3} to hundreds of μW cm^{-3} [39]. From the analysis of heat exchanged and other properties of TE and PE effects, it turns out that even though the power generated by PEGs is low, their efficiency is much higher than that of TEGs. A complete analysis of PE efficiency for each of the cycles here introduced can be found in the work of Batra *et al.* (2013)[47]. A more detailed explanation of the phenomena and its exploitation in some PE nanogenerators can be found in the work of Thakre *et al.*[48]

3 Emerging technologies

Several advanced, emerging technologies in WHP/WHR field have not been included in the previous section, for example: Trilateral Flash Cycle (TFC), Supercritical CO_2 (SCO_2) Brayton Cycle, magnetocaloric and thermomagnetic hydrodynamic machines. Other solid state emerging technologies such as Thermo-PhotoVoltaic devices (TPV) and ThermIonic devices (TI) have been discarded, as their description is beyond the purposes of the present review.

3.1 Trilateral Flash Cycle

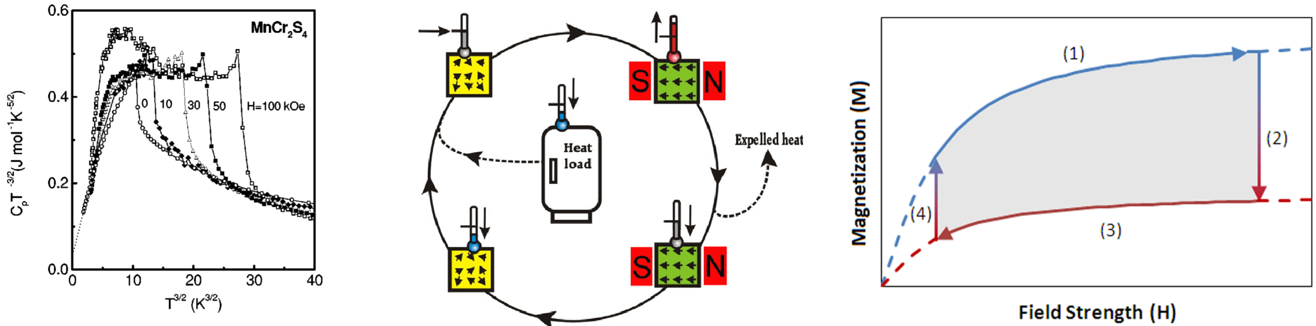
The TFC is a promising technology, having a huge recovery potential in comparison to ORCs, since the energy recovered can roughly double, over the same temperature difference; an economic outcome of this efficiency is related to the savings generated by avoiding any cooling/heat rejection system in a power plant. A TFC consists of a modified ORC where the organic working fluid is heated up to the saturation temperature under high pressure rather than evaporated, implying that the heat transfer is optimal when no fluid is brought across its boiling point. TFC-based systems can substitute more conventional ORC units installed in MT 70 and 200 °C processes, and they are able to follow any temperature variation both on the inlet and outlet phases of the cycle.[4,49]

3.2 Supercritical CO_2 Brayton Cycle

The SCO_2 BC is a standard thermodynamic cycle operating with CO_2 as working fluid. It is the power conversion system which combines the advantages of both Steam RC and GT systems. In other words, the fluid is compressed in the incompressible region and the higher turbine inlet temperature can be utilized with no material related issues in comparison with the SRC. As known, CO_2 is able to sustain dramatic density variations as a consequence of slight temperature and pressure fluctuations, granting an excellent energy extraction at HT, increasing the energy per kg/per m^3 of installed plant, one order of magnitude below steam/gas turbines. SCO_2 systems are mainly used in the HT end of thermal spectrum, for direct WHR, driving an electrical power plant or for both uses. Considering that the heat rejection also occurs at high temperatures, other systems such as a properly matched ORC could be cascaded. The most typical application is energy generation from geothermal sources, accounting for almost 75 % of world installed capacity. As can be noticed, taking into account the amount of installed systems, the diffusion of SCO_2 is quite limited, due to the capital intensive requirements that make reasonable its use in multi-MW power plants. The free market features a few technology providers (ORMAT, owning about 75 % of installations, Exergy with 13 %, TAS with 6 % and Turboden with 2 %), while a number of smaller providers cover the niche of small WHR plants ranging from 10 to 150 kW. A relevant fraction of these units are very small (<4 kW) plants installed by ORMAT for valve operation and cathodic protection along pipelines in remote areas.[49]

3.3 Magnetocaloric machines

A magnetic colloid (a suspension of magnetic nanoparticles in a liquid carrier), is a system where magnetization is thermodynamically coupled with temperature, at equilibrium. This aspect is at the basis of the so called Magneto-Caloric Effect (MCE): at rest and at a specific temperature, in a magnetic material some energy is transferred from phonons to the magnetic domain structure; if an external magnetic field is applied adiabatically, the magnetic domains align and reduce their number (entropy is consumed), and when the field is removed, in absence of energy exchanges with the environment, the material cools down. This effect has been discovered for the first time by Emil Gabriel Warburg[50], and is an intrinsic property of all materials. Considering a sample of ferromagnetic material, for example $MnCr_2S_4$ crystals, whose magnetic specific heat is shown in Fig. 6a. The following refrigeration process, called adiabatic demagnetization and shown in Fig. 6b, can be applied. Starting from top-left, the sample is at thermal equilibrium with the surrounding environment and the magnetic dipoles are randomly oriented, since no magnetic field is present; then a magnetic field is switched on, and the sample starts heating up, while the dipoles become aligned in the direction of the applied field. Subsequently heat is transported to the surrounding environment by means of a heat-transfer medium (the dipoles are still



(a) Magnetic specific heat for $MnCr_2S_4$ **(b)** Magnetic-refrigerating cycle **(c)** Thermomagnetic generation cycle

Fig. 6 Fig. 6a represents the specific magnetic heat for a ferromagnetic material, in this case $MnCr_2S_4$ crystals. Reproduced under the terms of the RNP/20/APR/024834 license.[51] Copyright 2020, American Physical Society. 6b shows the magnetic-refrigerating cycle related to magnetocaloric materials in general. Reproduced under the terms of the 1028944-1 license.[52] Copyright 2020, IOP Publishing. Finally, 6c represents the thermomagnetic generation cycle, featuring magnetization (1), heating (2), demagnetization (3) and cooling (4). Reproduced under the terms of the 4810850356977 license.[53] Copyright 2020, AIP Publishing.

aligned), but when the external magnetic field is removed, the dipoles' orientations randomize, which translates into a further temperature reduction of the sample (below the temperature of the thermal bath). Possible heat-transfer materials are water, or for very low temperatures, liquid He.[54] Furthermore, the (remanent) magnetization of a ferromagnetic material is a function of temperature. Under static magnetic field, cycling the temperature produces cycling of magnetization, in turn. The interaction between fluctuating magnetization and static magnetic field produces magnetic forces acting on the ferromagnetic (or superparamagnetic) particles that can be profitably converted, for example using extraction coils and induction principle, into electromotive force for electric powering.[53] A representative thermodynamic cycle for active thermomagnetic generation is shown in Fig. 6c.

3.4 Thermomagnetic Hydrodynamic machines

Magnetic colloids, such as FerroFluids (FFs), are nano-materials that present high magnetic susceptibility (some orders of magnitude higher than other non-magnetic natural substances).[55] In fact, when no external magnetic field is present, magnetic moments are randomly oriented inside the carrier fluid, and the resulting net magnetization is equal to zero. Otherwise, if the external magnetic field is present, the dipoles align along the direction of the field, and a non-zero net magnetization appears. FFs can be used to harvest energy, giving the possibility to implement a low-power micro-generator, especially suitable for electronics where battery replacement has higher costs and is quite difficult to be performed.

Furthermore, magnetic colloids show variations in the thermal convection due to a competition among the magnetic field and the gravitational one. In particular, when magnetic forces act in a direction transverse with respect to the gravitational field, which induces sedimentation of the colloidal magnetic particles by the effect of fluid density stratification, useful configurations arise. As said, in presence of an external magnetic field and a thermal gradient, FF shows the so called thermo-magnetic advection which induces different magnetic body forces (the cooler particles present an higher magnetization than the warmer ones).

In literature several methods to harvest energy using a FF are described, in particular from a thermal gradient: [56] describes a way to produce electrical power by exploiting the FF motion activated by convection currents generated by a thermal gradient. Furthermore, it is possible to generate solitonic density waves inside a closed loop system wrapped with copper wire coils, in order to extract electromagnetic forces and electric power, giving birth to the first generation of colloidal energy harvesters. [57] In all the cases where the gravitational field is parallel to both the thermal gradient and the external magnetic field, it is possible to exploit the Benard-Marangoni convection and extract energy through the use of coils, as reported by Kemkar et al. [58]

4 Industrial applications

4.1 Introduction

According to the IPCC, nowadays one third of the global energy consumption is employed in industry and this amount corresponds approximately to over 40 % of CO_2 emissions worldwide.[59,60] UK data show that industries absorb about $3,200$ TWh per year, which represents about 26 % of the total consumption in EU (Eurostat, 2015). Germany, Italy, France, UK, and Spain respectively, as expected, account for the highest industrial energy consumption, totalling about 60 % of all EU numbers.[61] Agathokleus *et al.* (2019) analyzed the energy consumption of the industrial sector of the EU28 (member states of the EU before Brexit)[49]: chemical and steel industries are the main energy-demanding sectors, followed by paper processing, non-metallic minerals treatment and food, and accounting for about 65 % of the total energy consumption in industry.

To manage the waste heat problem the most adopted approach is WHR. In a WHR device heat is exchanged between the diathermal material (which is cooled) and another intermediate fluid (which is heated). Such intermediate fluid is never dumped but recovered, and used to produce utilities such as steam or power.[49] Industrial WHR addresses temperatures ranging from 60 °C (cleaning processes) to more than 1700 °C (iron and steel, cement, glass and ceramics-processing industries). In chemical industry, the typical temperatures range is from 100 to 500 °C (in some cases up to 1000 °C).[6]. WHR technologies suffer from long payback periods, higher investment requirements, several additional requirements in terms of materials and design due to chemical activity and corrosion and as such they have been introduced in specific situations without wider diffusion. Nevertheless developing countries (hosting more than 4 billion people) are experiencing an ongoing industrialization process and could take advantage of experiences and technologies developed in more advanced countries. For sure, the industrial WHR/WHP will definitely be under the spotlight for the next years.[4] In Fig. 7 several industrial processes are associated to the corresponding temperature range while the complete

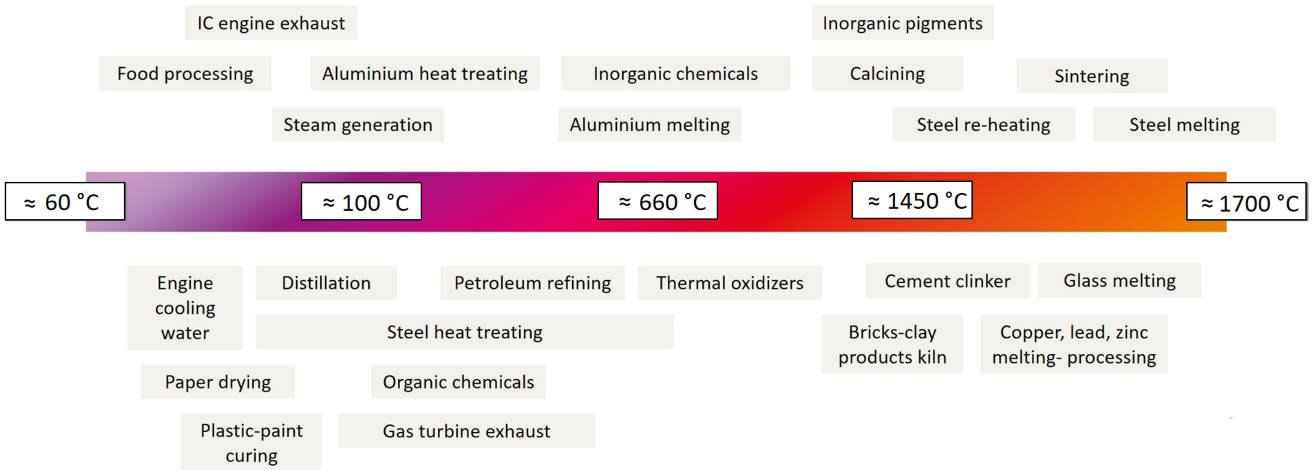


Fig. 7 Temperatures range for different industrial heating processes.[5]

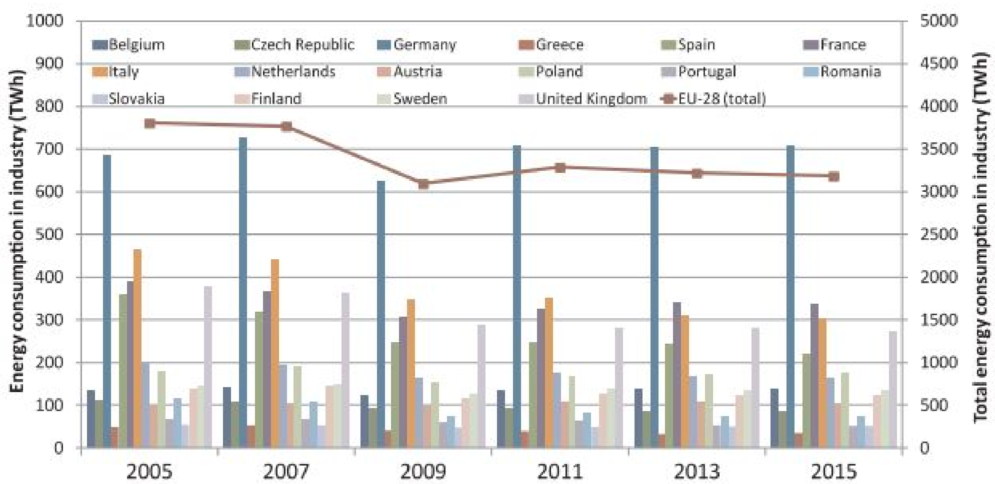


Fig. 8 Waste heat potential in each EU country per year in all industries. Reproduced under the terms of the 4811241236352 license.[61] Copyright 2020, Elsevier.

mapping of the potential of waste heat considering EU countries is shown in Fig. 8[61].

4.2 Technical potential of the waste heat from industrial activities

Among the various industrial sectors, the amount of waste heat fraction (with respect to the total energy consumption) can vary significantly. According to Agathokleus *et al.* (2019), the largest amount of waste heat is found in food and tobacco processing, pulp and paper processing, basic metals industries, chemical industry and non-metallic minerals processing, and 50 % of waste heat is in the temperature range between 300 - 350 °C.[49] Metallurgy and non-metallic

Table 1 Waste heat potential percentage per industry sector in Europe.[61]

Industrial sector	Heat consumption (TWh)	Waste heat (%)
Iron and Steel	580	11.4
Chem and Petrochemical	600	11.0
Non-ferrous metal	115	9.6
Non-metallic minerals	390	11.4
Food and Tobacco	345	8.6
Paper Pulp and Print	395	10.6
Wood and Products	100	6.0
Textile and Leather	50	11.0
Other	660	10.4

mineral transformation industries in U.S.A. are wasting 20 – 50 % of the energy used. McKenna and Norman (2010) conclude that the recovery potential for energy intensive industries in the UK is around 10 % of the total heat quota.[62] Waste heat potential in the EU has been estimated to lie above 350 TWh/year, the greatest part falling in the 100 and 200 °C range. Waste heat below 100 °C represents a marginal portion, while within the 200 and 500 °C range more important quantities are found.[61] This is an important amount of energy compared to the 3,218 TWh energy consumption of 2016.[61] Papapetrou *et al.* (2018) developed a statistics related to the waste heat potential in percentages per industry sector for all the former countries belonging to EU28.[61] The results are reported in Table 1.

4.3 Technology overview

4.3.1 Thermodynamic machines

To date, there is a consistent number of ORC manufacturers (Turboden, Opcon Powerbox, Orcan and EXERGY) and commercial applications in industry sectors. Leaving to the reader the disclosure of the manufacturer through the references given, as examples about ORC units operated by iron and steel foundries there are: the Fonderia di Torbole (Brescia) in Italy, which hosts an ORC plant since 1996 updated in 2018 and producing 690 kW; Toscelik Hot Strip Mill in Turkey producing 1 MW since 2011; NatSteel in Singapore with an installed plant producing 555 kW since 2013; Elbe-Stahlwerke Feralpi in Germany producing 2.7 MW since 2013; ORI Martin in

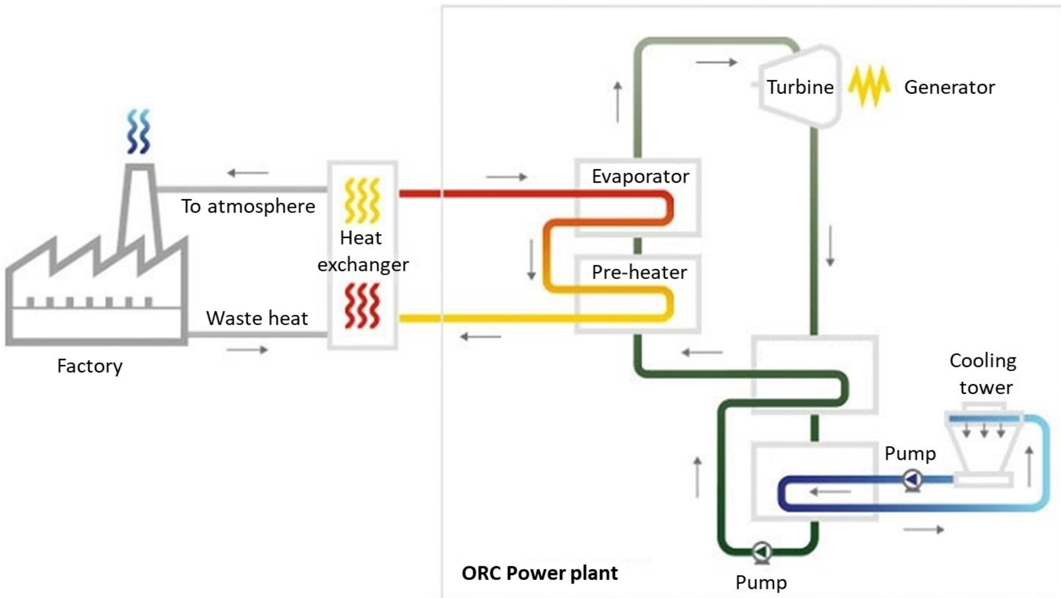


Fig. 9 Schematic of ORC installation in an industrial plant.[63]

Italy which converts 1.9 MW since 2016; the Munksjö pulp mill in Sweden producing 750 kW since 2010; the glass manufacturing plants of Sisecamin in Ostellato, Porto Nogaro and Manfredonia in Italy, which shares a capacity of 5 MW since 2016 for each of the locations. A cement plant in Lengfurt, Germany, burns around 3,150 tons of clinker per day in a rotary furnace at flame temperatures of about 2000 °C. This generates hot furnace exhaust gases (350 °C, heat flux around 8 MW) and waste heat from the clinker cooler (275 °C, about 60 MW). Part of this heat is injected back into the furnace. Until the ORC system has not been installed the remaining part of about 30 % was wasted into the atmosphere. In Fig. 9 the schematic of an example of ORC installation is shown.

KCs can recover industrial waste heat in the range 80 to 400 °C for power generation. Existing industrial WHR applications include: Sumitomo plant in Japan with an installed plant producing 3.5 MW since 1999; Husavik, Iceland plant which converts 2.0 MW since 2000; Fuji Oil plant in Japan converting 4.0 MW since 2005; DG KHAN plant in Pakistan converting 8.6 MW since 2013; Star Cement plant in Dubai producing 4.75 MW since 2013. KCs are limited in their industrial applications for some technical issues that have not been solved, yet, in particular the need for a fine tuning of the boiler evaporation ratio and the early condensation of NH_3-H_2O mixture.[1]

Solid Oxide Fuel Cell (SOFC) is considered an emerging technology for both small and large power plants for high efficiency power generation with low emissions. A comparative analysis in terms of energy and exergy has been conducted, for employing ORC and KC for waste heat recovery from hybrid SOFC/GT systems. The results show a good motivation for employing ORC or KC for WHR to increase the global energy conversion efficiency. The results indicate the superiority of ORC over KC.[64] A comparison of performances between KC and transcritical ORC for WHR in different internal combustion engine working conditions. Compared to KC, the transcritical ORC shows evident advantages on the overall thermodynamic efficiency, low operation pressure and simple components configuration with exhaust temperature from the engine over 220 °C. The optimal thermal performance of the transcritical ORC is in the range 295-345 °C. Nevertheless, moving over or under the optimal temperature drop the performances decrease considerably. Moreover, the extremely high expansion ratio of the turbine requires a complex multi-stage design and large dimensions.[65] Another comparison between the thermodynamic performances of KC and ORC has been conducted for the case of heat recovery from two Diesel engines, each one with an electrical power of 8900 kWe. Supposing a mean temperature difference in the heat recovery exchanger of 50 °C, a net electric power of 1615 kW and of 1603 kW can be generated, respectively, for KC and ORC. Although the output levels are almost equal, KC requires a much higher maximum pressure in order to obtain high performances. Then, at least for low power level and MT and HT thermal sources, KC appears to be unjustified because the increase in performances is very small (with respect to a properly optimized ORC) and must be obtained with a more complex plant scheme, larger surface heat exchangers and particular plants featuring pressure and corrosion resistance.[66]

In the last decade, the development of innovative thermodynamic cycles has been fundamental for the efficient utilization of low temperature heat sources such as solar, geothermal and waste heat sources and many researchers started to explore these technologies. Padilla *et al.* (2010) analysed a hybrid power/cooling cycle, which combines RC and absorption refrigeration cycles, using ammonia-water mixture and generating power and cooling at the same time. Also known as the Goswami Cycle, it can be employed as a bottoming cycle using waste heat from conventional power cycle or as independent cycle using solar or geothermal energy. The results show that with a heat source temperature between 90-170 °C and the absorber temperature of 30 °C, the maximum First Law efficiency (ratio between the net output power and the heat absorbed from the high temperature source to produce it) and exergy efficiency are estimated to be 20% and 72%, respectively.[67]

Nowadays, the number of commercial applications is very limited, even though industrial waste heat is available in abundance and the concept of utilization or recovery is not new. The reasons are mainly related to resource constraints and the insufficiency of regulatory, organizational and business plans.[1]

4.3.2 Thermoelectric devices

Several industrial companies have focused on TE technologies since these devices can compete with fluid-based systems, like compressors or heat pumps. Furthermore, solid-state energy conversion is more appealing because of its simplicity, if compared with compressing or expanding two-phase fluid systems. Although their limited efficiency, several commercial uses have been realized. The reasons behind this success are the relatively small size and complexity, vast scalability, robustness, rapid response time, lack of toxic operational emissions, long reliability and lifetime, inertness and lack of moving components[27,37]. Many countries, such as U.S.A., U.K., Australia, Ukraine, Japan and South Korea, are focusing their attention to this field[68,69] and several researches have been already accomplished to characterize the TEGs performances under various heat sources like diathermal oil heaters, cook stoves and waste heat from industrial process. The Aerospace, Mechanical and Manufacturing Engineering School at the RMIT University of Melbourne, Australia introduced the concept of hybrid power generation system.[70]

This is composed of one TE module hold by two copper layers with 4 heat pipes generating the temperature difference between the two TEG sides[70]. Another application of TEG modules is in support of the Industrial Wireless Sensor Networks (IWSNs), clusters of wireless sensor nodes in industrial plants and commercial areas. They consist of a high number of sensor nodes, including sensor units and control electronics, communication and power supply. Most of these are powered by means of batteries having strong limitation in terms of energy because of the constrained node and battery size. Therefore, several researchers explore the possibility of coupling IWSNs with TEGs in order to harvest energy and extend batteries lifetime, achieving higher power densities with respect to other energy harvesters. It has been concluded that, with 0.6 m/s of air flow on the TEGs and without using any heat sink, the hot side being at 50 °C and the cold one at 20 °C, the output power is around 80 μW. Dalola *et al.* (2009) used a TE component to supply an autonomous sensing node for T measurement.[71] Bonin *et al.* (2013) produced and characterized small TE generators used to power systems for environmental monitoring, in the order of 10 mW for a temperature difference of 10 °C.[72] In another application domain, 52 % of Australian households hot water heaters are powered by using natural gas and Liquified Petroleum Gas (LPG) systems. By exploiting the thermal gradient generated between hot exhaust gas exiting and cold water from ducts, it would be possible to generate power by means of TEGs. Through the testing conducted, a power generation unit including 60 TE cells would be able to produce more than 40 W and more than 20 W in case the hot water is around boiling temperature and 80 °C, respectively. In the latter case, the efficiency of the system is estimated to fall in the range 0.37 % to 1.03 %.[73]

Furthermore, some hybrid concept and devices have been analysed. Gholamian *et al.* (2018) focused on enhancing the performances of a geothermal-based ORC and proposed two novel systems in which, in the first case, part of the waste heat is recovered employing a TEG for power generation while in the second for hydrogen production (by means of proton exchange membrane electrolyzer). Results indicated that the proposed system has exergy efficiencies higher than that of the basic ORC by 21.9% and 12.7%, respectively. They also reveal that the specific product cost for the proposed solutions is lower than that for the basic ORC, despite an higher total cost rate.[74] Zare *et al.* (2017) studied the possibility of employing TEG to recover the waste heat from a KC and the results revealed an improvement of around 7.3 % of the net output power and higher energy and exergy efficiencies. Furthermore, they evaluated economically the integration of TEG with the KC indicating a modest profitability.[75]

4.3.3 Novel approaches

Recently, innovative method for low-grade waste heat recovery based on nanogenerators have been deeply investigated and, even though a large margin for improvements is still present, some interesting results have been reached. To be mentioned is the work of Raouadi *et al.*[76] where an hybridized pyro-vortex device, realized in polyvinylidene fluoride (PVDF), has been realized, with an area of 2 cm^2. The idea behind this work is to exploit the energy of the wind to realize an inexpensive and efficient harvester providing an uninterrupted energy output. In particular, the vortexes generated by this latter give rise to two conversion mechanism: molecular transport, proportional to the gradients of the averaged velocity of the wind and heat fluxes, and convective transport, who gives rise to turbulent stresses caused by the momentum transfer produced by the velocity fluctuations. In fact, this device allow to produce a stable output current reaching a maximum power density of 2.82 μW/cm^2.

The flexible device developed by Chen *et al.*[77] is based more on mechanical solicitation instead of temperature variation. In this case, the mechanisms of conversion are piezoelectric and triboelectric, i.e. relying in deformation and friction processes, respectively. The energy to be harvested can be associate to different sources and the device results suitable for many application. As an example it can be thought as a device to be inserted in the floor or, thanks to its dimensions, for biomedical applications supplying sensors for health monitoring, converting the energy coming from the motion in electricity, e.g. placing it under the shoes. The maximum power produced in this case reached 0.834 μW/cm^2.

A combination of pyroelectric and triboelectric hybrid energy harvester has been also proposed in the work of Jiang *et al.*[78] where the idea is to harvest useful energy from low-grade waste fluids. In practice, the drops of fluid can be make fall onto the device surface and energy can be recovered exploiting both their thermal and kinetic energy. In fact, the drop hitting the surface will release its energy on it, provoking friction and thus the triboelectrification to take place, but also have a certain temperature that will provoke temperature variation, allowing pyroelectrification. The maximum power produced per unit area similar to the one proposed by Rouadi, lying around 2.6 μW/cm^2. Interesting is to notice that all these devices have been realized in PVDF, which seems to be a promising material in LGWH harvesting, and are solid state.

Two innovative works propose a liquid-state low-grade waste heat harvester. The idea is to combine solid and liquid properties, realizing a stable suspension of nanoparticles in a carrier fluid, and move this mixture by means of a combination of thermal and magnetic flux gradient. This thermomagnetic motion will allow the nanoparticles to crawl on the walls of the container, provoking charge accumulation by means of triboelectric process,[79] and to experience a temperature variation in time, provoking pyroelectrification[80]. At the state of the art the device has been tested only in laboratory and still need some improvements to be reproduced in large scale. However, the results are encouraging and the possible application are various since the device, until now is proposed in two shape, i.e. toroidal or planar, and can be applied on whatever hot surface.

5 Automotive applications

5.1 Introduction

Road freight vehicles and passenger cars play an essential role in today global economic activity, energy consumption and environmental impact. According to the International Energy Agency (IEA), transport accounts for more than half of oil global demand, totalling around 52 million barrels of oil per day (mb/d) ¶.[81] Furthermore, IEA estimates that the global fuel consumption for high-duty vehicles is increasing more rapidly than any other transport mode, especially in emerging markets such as India, China and Latin America.[81] In view of the Paris Agreement, countries have been considering different solutions to secure improvements in transport efficiency and emissions reductions, both for light-duty vehicles (LDVs) and heavy-duty vehicles (HDVs). In response to this energy and environmental challenges, the automotive industry is focusing on high efficiency vehicles. According with the Global Fuel Economy Initiative objective, within 2030 LDVs should improve the fuel economy by 50 % and save 0.5 Gt of CO_2 emissions per year.[81] Nowadays, the principal path towards a sustainable transportation is the electrification and hybridization of automotive powertrains, while industry is also focusing on different technical solutions to increase the fuel efficiency of Internal Combustion Engines (ICE) vehicles.

5.2 Mechanical and Thermodynamic analysis

Sovran and Blaser[82] (2003) proposed a complete physical analysis of fuel consumption in an automotive system, indicating that 58 % of the traction power at the wheel is lost due to vehicle inertia in an urban driving condition. On the contrary, aerodynamic losses become dominant in highway driving conditions (50 % of the traction power at the wheel). The U.S. EPA City and Highway Driving Cycles provide an energy loss analysis based on the energy utilization in different driving conditions and different size-mass vehicles (Fig. 10). It is interesting to note a lost in fuel energy around 35 % and 30 % in exhaust and coolant[83,84] gases respectively,

¶ Considering Barrel of Equivalent Oil (BOE), it is possible to say that the transport sector has an energy demand of 88 TWh per day.

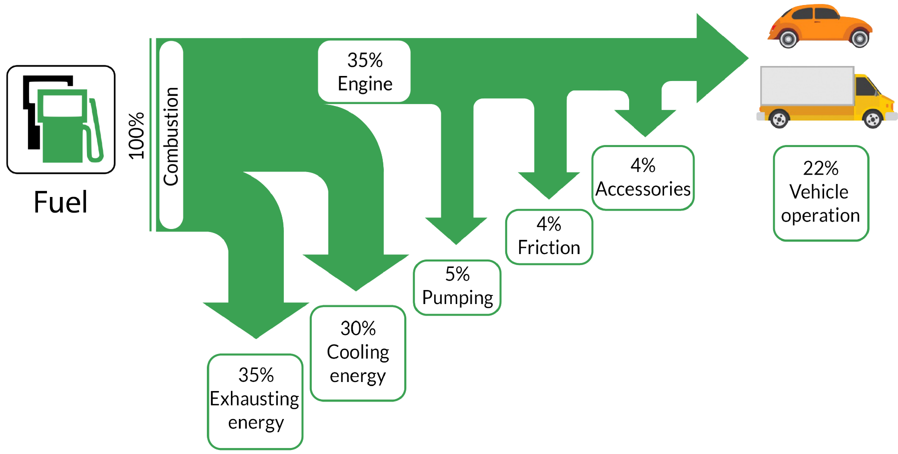


Fig. 10 A Sankey diagram showing the fuel energy utilization of an ICE.

representing more than half of losses in wasted heat form. Nowadays, engine manufacturers are concentrating on two different ways to increase the thermal efficiency of an ICE. The first one focuses on improving the thermodynamic cycle of the engine, operating on the choice of fuel, combustion system and air-path. For example, downsized engines deployed in production vehicles improve the fuel economy by $8-10$ % for LDVs in urban pathway.[85] The drawback of this approach consists in a reduction of available power and in an increase of fuel consumption, especially in highway conditions.

The second trend concerns WHR and WHP. WHR has the important feature to not affect the engine design and technical features of the vehicle, since it uses the heat rejected by combustion. Therefore, it is suitable for different driving conditions and it can be easily integrated. However, the key point of this technology is to guarantee competing requirements of costs, engine durability and emissions.[86]

By considering detailed models and simulations of the thermodynamic behaviour in an ICE[87,88], it is possible to conclude that the exergy loss (or availability loss) is mainly originated by irreversible combustion processes and the energy is mainly conveyed by exhaust gases. This suggests that the best option to maximize the energy recovery is to install the recovery plant in close contact with the exhaust gas ducts or to the cooling system.

A further important feature is thermal availability, or rather the entropy maximization, representing the maximum amount of work necessary to establish equilibrium in the system[89]. This concept is closely related to heat grade (temperature). While HT and MT conditions are widely used for practical power generation, LT sources represent today's challenge in the automotive industry. LT sources are mainly localized in the cooling systems (radiator and air conditioning) and in exhaust gases exiting other recovery devices.[90]

5.3 Technological Overview

From a historical point of view, the first approach adopted in WHR for the automotive field is the Mechanical Turbo-Compounding (MTC). This technique employs a turbine to extract energy from HT/MT thermal energy (from 400 to 600 °C[91]) using the combustion gas streams. At present, Detroit Diesel, Iveco, Volvo and Scania truck manufacturers produce engines that make use of this recovery technique. MTC technology is essentially based on the concept of additional heat by a second exhaust turbine from a turbocharger: instead of ejecting the excess of energy via the exhaust pipe, it is possible to extract additional heat by using a second exhaust turbine. The rotational motion passes through a gear system and a hydraulic coupling, boosting the torque available on the crankshaft. This permits to have extra driving force without additional fuel expenditure. Several studies show that MTC improves the thermal efficiency from 3 % to 5 %.[92] The main disadvantage of this technology is that MTC design expects the interaction of the recovery system with the engine, generating an exhaust back-pressure. This makes it suitable only for HDV industry. The ICE cooling system is the most promising area of investigation to exploit LT recovery.[93] The low mass flow rate of the working fluid can guarantee the realization of smaller size recovery systems.

5.3.1 Organic Rankine Cycle

In the automotive research field, all the bottoming cycles described in previous section (ORC, SC, KC and BC) are under investigation. In particular, ORC is the most economically advantageous for WHR when the thermal source is below about 150 °C.[95] It is also very attractive for mass-production, because of the low-cost, the easy integration with the cooling system (where the

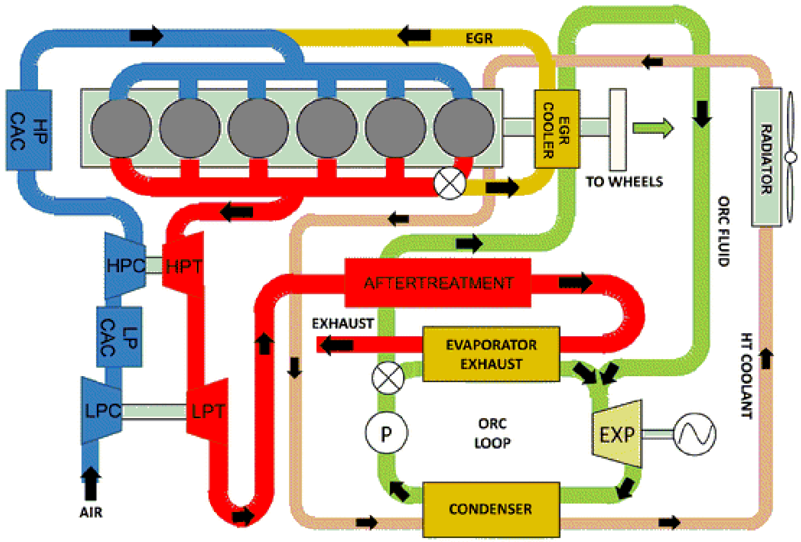


Fig. 11 Model of ORC in an automotive system. Reproduced under the terms of the Attribution 4.0 International license.[94] Copyright 2017, Springer Nature.

working fluid temperature ranges from 60 to 90°C) and the low impact on engine design. The industrial groups that are currently investing in research and development in this area are BMW, General Electrics, Cummins Engine and United Technologies Corporation.

An ORC permits to exploit LT sources in a very efficient way.[96] In Fig.11 it is possible to observe a standard configuration for automotive applications. The design challenge consists in the miniaturization of the expander machine[97] which operates with organic fluids.[98] This is important to reduce the weight-to-power ratio of the dynamic machine[99] decreasing the inertia of the vehicle. The operation conditions of the ORC can be dived in direct and indirect. In the direct recovery method, it is possible to use the engine block as heat exchanger, avoiding specific heat conversion parts of the cooling system.[100] This means that higher T can be exploited in WHR system, hence it is possible to use more heat rejected by the ICE. Other studies show how the heat dissipated by the engine block can be coupled with the vaporizer cooling system. Doing that, it is possible to recover about 3 % of output energy of the engine.[101] In indirect harvesting procedures, heat is transferred from the coolant to the ORC working fluid by using an extra heat exchanger. Several studies[102–105] show how the heat dissipated by the coolant fluid can be used for the evaporation system or as a preheater for a HT Rankine-Hirn cycle. In this second case, it is possible to reach higher efficiencies,[106] but the system is heavy and cumbersome, therefore economically unfavourable for automotive applications.[91] Other approaches[107] involve the use of the heat rejected by the cooling system for the confluent cascade expansions ORC system.

The matching conditions between working fluid and ORC systems is investigated to make the cooling system absorb the whole waste heat. In LT recovery systems organic fluids with low boiling temperature and low freezing temperature are used. In fact, these characteristics allow the absorption of the low T heat in the RC system. However, it is difficult to keep a high mass flow, since the organic fluids have inherently a low stability at high temperatures and low specific heat. One option to increase the efficiency is sizing a larger recovery system (as in industrial plants). Another solution could be using high specific heat fluids, like water. Other important features that affect the recovery efficiency are thermal fluctuations, due to changeable driving conditions. Jimenez-Arreola *et al.* (2018) give a general overview on these effect. This phenomenon negatively affects the WHR systems, limiting the operational range and inducing an efficiency drop during partial load. A possible solution is represented by stream control, used to ensure a close and safe optimal point operation.[108] Pili *et al.* (2017) analyzed the economic impact of the ORC technology in transportation sector. They considered the relationship between WHR that impacts the net fuel economy of the vehicle and the costs of additional volume that the ORC system occupies, affecting the vehicle transportation capacity.[109]

5.3.2 Thermoelectric Generators

Another possible way to improve the vehicle efficiency using WHR system is to exploit the TE effect. TEGs allow to recover heat from ICE in order to reduce fuel consumption, without increasing emissions. BMW, Nissan, Jaguar, Land Rover and Porsche are some of the manufacturers that are investing in this field. Exhaust TEG (ETEG) is the most promising technology, because it has no moving parts, it requires less maintenance in comparison to ORC and MTC systems and it is silent in operation.

Despite the lightweight of ETEG and its versatility, the technology must address a number of

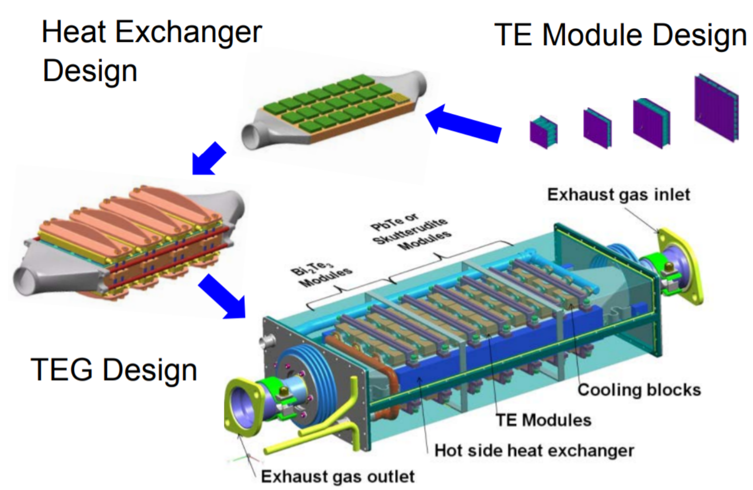


Fig. 12 Example of ETEG design.[110]

issues such as low efficiency (5 % to 10 %), high cost and large temperature differences required for considerable energy conversion. In particular, the cold side of the ETEG module should be at a temperature as low as possible to maximize the efficiency. Therefore cooling mechanisms are required to provide the maximum temperature gradient. In a typical ICE, the ETEG is composed by 4 units: a TEG module, a heat sink, a heat exchanger and a power conditioning unit (PCU). An example is shown in Fig. 12. Exhaust gases pass through the heat exchanger placed on the exhaust pipe, causing an increase in temperature on the warm TEG modules side. The other side can be refrigerated using a liquid or an air cooled heat tank system. The generated electric power due to the temperature difference established across the TEG module is stored in a battery, matched with the vehicular electrical system through a PCU.[111,112] This latter is essential in order to guarantee the maximum power transfer in different driving conditions (idle or operational).

Komatsu (Japan), Marlow (USA) and HiZ (USA) produce and commercialize TEG modules using Bi_2Te_3 as active material. In particular HiZ produces several devices that work with a maximum temperature of 250 °C and a ΔT of 200 °C, producing from 2 to 20 W of electrical DC power. The cost of these devices can range from 18 EUR to 80 EUR per module, depending on dimensions and on purpose.

It is important also to focus on the installation position of TEG device, since the heat exchange efficiency plays a fundamental role. In general, it is possible to adapt both size and shape of the TEG module according to the recovery application: for example in the case of exhaust pipes a square configuration can be chosen for flat surfaces, or a linearly shaped one for circular pipes. Liu *et al.* (2014) tested different installation positions of an ETEG, finding that for LT applications the best solution is positioning modules after the catalytic and filtering blocks the exhaust system.[113]

An interesting experimental study[114] shows that using six Bi_2Te_3 TEG modules on a 3,696 c.c. gasoline engine having hot and cold sides at 225 °C and 255 °C respectively, it is possible to generate an output power of more than 40 W. In accordance with other researches[115,116] the fuel economy of a vehicle can be improved up to 2 % using LT exhaust gases.

A different approach for WHR is proposed by Park, Yoo and Kim (2010).[117] As in the ORC case, they recover energy from the engine coolant, substituting the radiator system with a system of 72 TE modules (Bi_2Te_3 with an area of 4mm $\times$ 4mm) and 128 heat pipes. The coolant flows inside a chamber where the squared modules are installed, transferring heat to the hot surface of the material and reaching 95 °C. To keep the temperature of the cold side at 25 °C, a standard air-cooling system has been used. Results show that it is possible to generate almost 30 W of electrical DC power during idle condition and almost 75 W during driving condition. This approach allows to recover 0.4 % of wasted heat.

At present, the cost of commercialized TEGs is in the range of 2,500 EUR/kW to 3,500 EUR/kW. In order to be competitive, the cost per energy capacity has to decrease at 395 EUR/kW.[118] Nowadays only HDVs can benefit from TEG systems, since it is easier to depreciate installation cost considering both the driving conditions (long driving distances) and the higher amount of energy from exhaust gases with respect to LDVs.

6 Wearable applications

During the last decades, technology has performed steps in the direction of an extreme miniaturization of electronic components and portable devices. In addition to devices for healthcare [119] and self monitoring of activities and vital functions [120,121], the production of electric energy from human body waste heat has become significantly important because of the rising of Ultra-Low Power (ULP) devices. [122] Despite the development of new supply technologies, researchers have started to explore a possible definitive solution: battery-less devices, integrating an energy harvesting system where mechanical load, vibrations, temperature gradients, heat, light, salinity gradients, wind, etc. are scavenged and converted to obtain relatively small amounts of power. Examples of this kind of device are thermo/tribo/piezo/pyro-electric effects. Of course wearable devices are not comparable with industrial or automotive applications in terms of energy produced, but still they are part of category of technologies able to convert waste heat into power, which moreover, could be explored in sport and space application field, where small amounts of power are enough to power smart devices.

6.1 Thermal energy harvesters

According to [123] the energy requirements of an average person under 60 years are in the range of 8.8 to 17.6 MJ per day (man) and between 7.1 to 14.2 MJ per day (woman) ††. Therefore assuming that on average the daily energy need is about 10 MJ and the corresponding power is $\approx 120\,W$, considering to radiate a large part of this energy in form of heat, a thermal source of some tens of Watts, at rest, is available [124]. Therefore harvesting even a small part of this energy would enable powering wearables such as smartwatches, that need a few tens of mW to operate [125]. Assuming a normal condition, that is a body temperature of 36.6 °C [126] and a room temperature of 27 °C, it is possible to estimate a Carnot efficiency of approximately 3%, which makes immediately clear the constraints for the application on a human body. However, even 1 % of a total power in the order of a hundred Watts still represents an amount of energy

†† The numbers reported here are obtained for a subject at rest (basal metabolism rate).

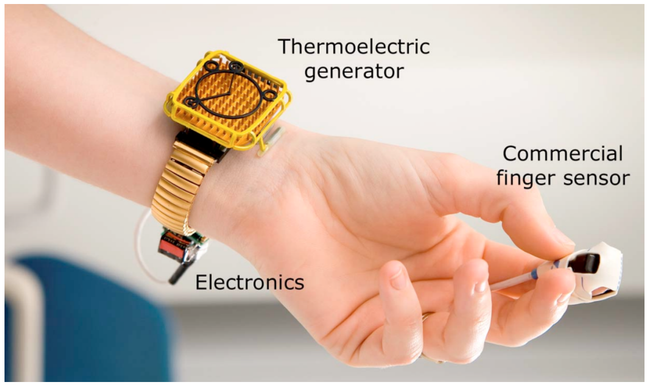


Fig. 13 Fully powered wireless pulse oximeter:[129] on the forefinger a commercial sensor has been placed. The wristwatch TEG charge a storage capacitor able to provide $0.7-2$ V as output voltage. A DC/DC converter to ensure stable and higher V_{oc} is mounted after the capacitor itself. A V$=2.05$ V is obtained, which is enough to supply the wireless sensor. Reproduced under the terms of the 4877660286134 license.[129] Copyright 2020, AIP Publishing.

sufficient to power wearables.

6.1.1 Rigid and flexible thermoelectric devices

The wearable TEGs (WTEGs) for LT waste heat scavenging do not use bulky material but rather thin layers of material. For this reason they are typically referred with the name μ-WTEG. Initially, rigid substrate TEGs have been the focus of research. Leonov *et al.* (2007) published a study on TEGs aiming at finding a smart way to maximize the energy scavenged, resulting in the employment of a multistage multistage thermopile[127]. Torfs *et al.* (2007) proposed a completely self-powered device to measure the oxygen content in blood.[128] It consisted of an oximeter for the measurement and of a wristwatch, disguising the TEG, providing the energy needed (an explicative scheme of the whole apparatus has been sketched in Fig. 13). The maximum power extracted is more than $100\,\mu W$ during daily activities. A year later, the same research group proposed an electroencephalography (EEG) system.[130] A battery-less device specific for EEG, ECG and EMG data transfer has been investigated by Zhang *et al.* (2013) few years later.[131]

More recently, the work presented by Wahbah *et al.* (2014) has opened a new way towards self-powered systems.[132] They characterized two different devices, a TE and piezoelectric energy harvesters, in order to find the best way to supply the system. They showed that a 9 cm^2

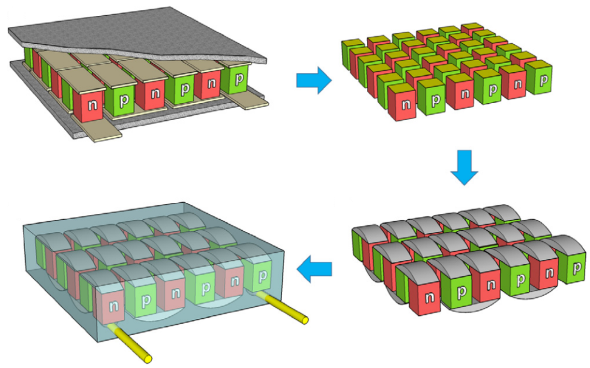
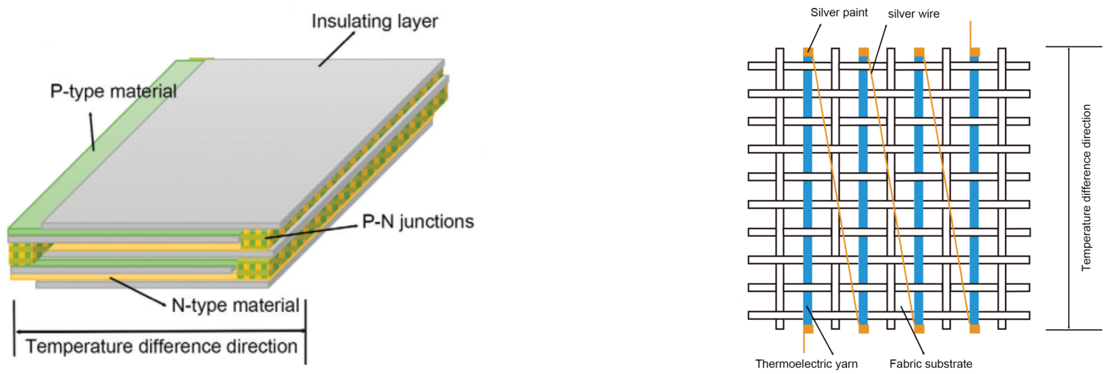


Fig. 14 Scheme of the transition from rigid to flexible device substituting the ceramic plates with liquid bendable connection. Notice that the legs are the same of the rigid device. Final step consist in an encapsulation in polydimethylsiloxane (PDMS). Reproduced with permission.[134] Copyright 2017, Elsevier.

TEG system is able to generate up to 20 μW at RT with respect to the 3.7 μW of a 5 cm^2 piezoelectric one. By properly setting the parameters, they reached $V_o = 12$ mV and $V_{oc} = 24$ mV for a of 0.5 °C, i.e. output and open circuit voltages respectively. The main drawback of rigid WTEGs is the incapability of following the curvature of human skin, with concurrent heat transfer losses. Moreover, the integration of a rigid wTEGs into clothes is not easy and makes them uncomfortable. For these reasons flexible devices have substituted the rigid ones as focus of research.

Concerning wearable applications, the problem of comfort is not the only one. The low temperature difference deeply affect the overall efficiency of the devices. Thus, to solve this issue, in 2017 an interesting way to increase has been explored by Soo Jung *et al.* in[133]. They propose to use a local absorber placed below the TEG legs (BiTe and SbTe) onto such layers, the temperature difference passes from the usual $2 \div 4$ to 20 °C. A prototype consisting of 10 p-n couples develops an output around 4.44 μW and a open circuit output voltage of 55.15 mV. However, it is possible that such local increase of temperature could results to be uncomfortable for the user but opens doors for possible future implementation in WTEGs.

It is important mentioning also the work proposed by Wu *et al.*[135] (2018) that tried to look for another way to integrate the harvesting system directly into the clothes' fibers. They have analysed closely the textile TE material from both application (monitoring, computing, waste



(a) Multilayer 2D thermoelectric structure.

(b) Thermoelectric 2D yarn arrangement.

Fig. 15 Arrangement of 2D textile thermoelectric device. In 15a a multilayer arrangement proposed by Hewitt *et al.* (2012) is reported. It uses n and p-type carbon nanotubes (CNT) separated by insulating PVDF films. In 15b a yarn structure proposed by Ryan *et al.* is shown (2017). This is a silk yarn made of PEDOT:PSS which ensures stability in performances also after washing and drying.[136]

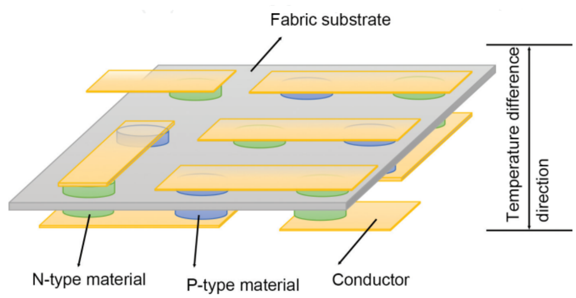


Fig. 16 Arrangement for a 3D textile thermoelectric generator proposed by Kim *et al.* in 2014. This kind of structure allow to sustain a temperature gradient along the thickness contrarily to 2D structures.[136]

heat recovery) and production (fabric finishing and coating or fibers/yarns coating technologies) points of view. These can be a very good alternative to other kind of devices thanks to the ease of integration, comfort and air-permeability. Their structure is different since does not rely on a sandwich design but on a planar one. This implies that the temperature difference is applied along the length and not the thickness of the leg for stability reasons. However, they can be arranged in either 2D (Fig. 15) structure or 3D one (Fig. 16)*

* The images has been originally published in IntechOpen under Creative Commons Attribution License by Qian *et al.* [135] and therein references. Available from: http://dx.doi.org/10.5772/intechopen.75474

6.1.2 Pyroelectric energy harvester

As already pointed out, the heat constantly flows out from our body because of self thermal regulation, i.e. the homeostasis process through which the body is able to maintain always an external temperature around 36 °C, in a range of about 1 °C. Moreover, the physiological rate of temperature changes is not so fast. Thus, it is clear that the efficiency of devices exploiting PE only is so low that makes them unsuitable for body WHR applications.

Nevertheless, Yan *et al.* [137] (2018) conducted a study on the possibility of using nanogenerator technology as a self-driven power supply for wearable devices. Here, it resulted that a combination of more effects, in particular tribo-electric and PE could be a good solution for solving the problem of powers supply. The performances of such hybridized nanogenerators have been investigate in [138].

Potnuru *et al.* (2014) proposed a mouse supplied using human heat exploiting just the PE effect. [139] They have found that the current generated by PE effect is so low that it is completely dominated by the one due to piezoelectric effect which is also intrinsic of those materials that have a PE effect, provoked by the weight of the user's hand. Sultana *et al.* [140] (2018) investigated a commercial PE device which is composed of a piezoceramic foil placed between two conductive electrodes. They prove the possibility to use water vapour to drive the device obtaining an output voltage higher (1.6 V) than in other conditions (0.4 V) thanks to the increase in T difference. The maximum output power obtained is 0.034 μW cm^{-2}.

Hybrid systems exploiting piezo and pyro-electric effects have been studied. [141] A very interesting hybrid device has been proposed recently by Ding *et al.* (2018) implementing a thermocell and a pyroelectric harvester which treats to recover heat by both stable gradient and temporal variation of temperature. [142] This device consists of two layer of poly (vinylidene difluoride) (PVDF), coated with CNT/CNC nanocomposites that serves as electrodes and absorber, and a block of polyurethane (PU), which is place under the two PVDF films. The former deals with heat recovery from T variation, thus is the PE part, whereas, once the temperature gradient is

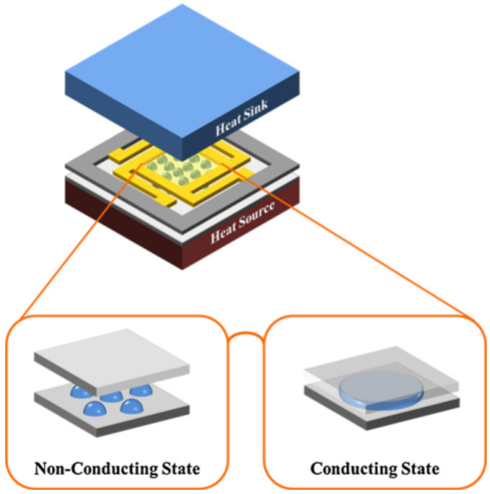


Fig. 17 Image of the Liquid-Based Thermal Interface device structure proposed by Cha *et al.* in[143], 2012. Reproduced with permission.[143] Copyright 2012, Elsevier.

established, in the thermocell a redox of ferrous/ferric chloride acid develops converts it in useful electric energy. Moreover, an analysis on performance versus the content of CNTs in CNCs is performed resulting in a verification of the crucial role played by CNCs. The thermogalvanic cell has shown a current density production of 1.2 A m^{-2} for a of 100 °C. Assuming an illumination of AM 1.5 G, the PVDF film generates up to 200 V of output voltage under illumination and −120 V once the illumination is removed. The importance of this device lies mainly in its versatility since it can harvest energy in difference conditions, being thus able to act as a supply 24/7. The hybrid has shown a maximum output power produced of 1.86 and 0.9 mW m^{-2} for the thermogalvanic and pyroelectric components, respectively. Recently, a wearable pyroelectric nanogenerator based on the breathing process has been proposed in the work of H. Xue *et al.*[144] where they successfully introduced a thin film of polyvinylidene fluoride (PVDF), of dimensions 35x35mm and thickness 30 μm, in a mask. Exploiting the heat released by the breath, the maximum temperature variation registered on the harvester was 12 °C and the maximum power extracted, with an external load of 50 MΩ, reached ≈ 0.68 μW/cm^2.

Finally, it is worth to mention a work proposed by Cha *et al.* (2012) dealing with liquid-based PEGs. They proposed a harvester based on PE effect but using a liquid based switchable interface.[143,145] The structure of their device is shown in Fig. 17.

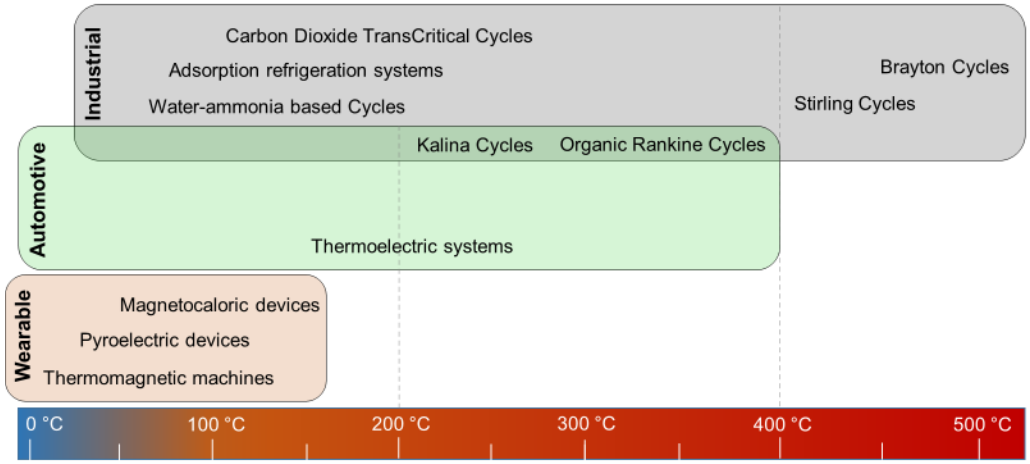


Fig. 18 Most of the technologies analysed, grouped according to their application field and optimal temperature range of operation. Note that this graphical summary is conceived only to give an immediate, qualitative glimpse on the statistics of technology application. For this reason, the reader should focus on the temperature ranges rather than on the specific temperature values.

7 Conclusions

The identified technologies have been collected and sorted according to their typical application and optimal temperature range in Fig. 18. A comparison in terms of efficiencies, post-installation costs per kW and typical installed power output is given in Table 2. The reader should never forget that closed loop thermodynamic cycles based on any specific fluid feature intrinsic installation costs that strongly limit their power output lower bound, while purely solid state systems such as TEGs and PEGs suffer from the specular limit, toward upper bound. Once the available WHP technologies have been analysed, question arises on whether they could represent a valid approach to increase the quota of "green" installed power, working both in conjunction with fossil fuel-based processes and renewable resources-based processes. Considering their costs per kW and comparing them to photovoltaic systems (on average the cost per kW is 1.4 kEUR/kW as of December 2018), two technologies are already competitive: BC and ORC. On the other side, the higher production costs of wind turbines (on average 1.4 kEUR/kW as of 2017 for onshore plants and 3.5 kEUR/kW for offshore ones), of biomass-based power plants (3.3 kEUR/kW),

Table 2 Efficiency and installation cost/kW comparison between the mentioned technologies.

	BC	SC^{c}	KC	CDTCC	ORC	TE	PE
η @ LT (T_{Hot} = 20-200 °C)	0.40^{a}	0.13	0.10^{d}	0.15^{f}	0.12^{g}	0.037	0.15
η @ MT (T_{Hot} = 200-500 °C)	0.40^{a}	0.20	0.15^{d}	-	0.20^{g}	0.073	0.13
Cost per kW [kEUR/kW]	1^{b}	12-2.5	6.5-2.5^{e}	N.A.	2.8-1.2^{h}	2.5	N.A.
Installed power [MW]	7.8^{i}	0.0015^{j}	0.4^{k}	0.0046^{l}	0.35^{m}	0.012^{n}	N.A.

In the above table, data relative to CDTCC is not given at MT due to the intrinsic properties of CO_2, implying that the cycle operates at cryogenic temperatures. The thermoelectric efficiencies have been computed by using conventional physical models and assuming reasonable temperature ranges in operating conditions (55 °C of ΔT for LT and 150 °C of ΔT for MT) and an average ZT FoM of 1.5 for LT and 2.5 for MT (on the basis of previously reported analysis). For pyroelectric efficiency data have been derived by[42] and the same temperature ranges as above have been considered. ^{a}[146]^{b}[147]^{c}[148]^{d}[149]^{e}[150]^{f}[151]^{g}[33]^{h}[152]^{i}[153]^{j}[154]^{k}[155]^{l}[156]^{m}[157]^{n}[158]

and of hydroelectric power plants (3.6 kEUR/kW), give already a strong evidence of the bright future this sector will experience, since at least some, if not all, the technologies here described could be potentially competitive.

In parallel to industrial development and technology readiness level, the most statistically relevant results in all ranges of reviewed current solutions, mainly involve optimization through thermoeconomic, exergetic and life cycle assessment analyses, as well as materials development. A totally different approach is seen for emerging technologies, where basic studies and theoretical developments are frequent. In conclusion, WHR/WHP technologies have reached a maturity level that could significantly boost their mass application in close relationship with industrial processes and wherever waste heat is generated, such as in the automotive field, regardless of the policies enforced at local/global level. Scientific research, on the other side, is rapidly expanding and casting light on less explored multidisciplinary fields, where combined effects (such as pyro + thermo + magneto) have been shown to greatly enhance conversion efficiencies and volume/mass specific power/energy. In particular, the most promising directions to explore are: 1) magnetocaloric and thermomagnetic hydrodynamic machines on the one side, and 2) thermoelectric, triboelectric and pyroelectric devices on the other side, the former group suitable for small scale systems and the latter suitable for wearables.

Conflicts of interest

There are no conflicts to declare.

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