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

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8 Abstract

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

24 discussed.

25

26

27 **Nomenclature**

- 28 • Barium Titanate (BT)
- 29 • Barrel of Oil Equivalent (BOE)
- 30 • Brayton Cycle (BC)
- 31 • Carbon Dioxide Trans-Critical Cycle (CDTCC)
- 32 • Carbon NanoTubes (CNT)
- 33 • Electric Turbo-Compounding (ETC)
- 34 • Exhaust ThermoElectric Generator (ETEG)
- 35 • Figure of Merit (FoM)
- 36 • Gas Turbine (GT)
- 37 • GreenHouse Gase (GHG)
- 38 • Heavy-Duty Vehicle (HDV)
- 39 • High Temperature (HT)
- 40 • Industrial Wireless Sensor Network (IWSN)
- 41 • Internal Combustion Engines (ICE)
- 42 • International Energy Agency (IEA)
- 43 • Kalina Cycle (KC)
- 44 • Lead zirconate titanate (PZT)
- 45 • Life Cycle Assessment (LCA)
- 46 • Light-Duty Vehicle (LDV)

- 47 • Liquefied Natural Gas (LNG)
- 48 • Liquefied Petroleum Gas (LPG)
- 49 • Lithium-Ion Battery (LIB)
- 50 • Low Temperature (LT)
- 51 • Magneto-Caloric Effect (MCE)
- 52 • Mechanical Turbo-Compounding (MTC)
- 53 • Medium Temperature (MT)
- 54 • Organic Rankine Cycle (ORC)
- 55 • Poly (3,4-EthyleneDiOxyThiophene) TolueneSulfonyl (PEDOT-ToS)
- 56 • Poly Vinylidene Fluoride (PVDF)
- 57 • PolyEthylene Naphtalate (PEN)
- 58 • PolyStyreneSulphonate (PSS)
- 59 • PolyVinyl Chloride (PVC)
- 60 • Power Conditioning Unit (PCU)
- 61 • PyroElectric (PE)
- 62 • PyroElectric Generator (PEG)
- 63 • Rankine Cycle (RC)
- 64 • Return On Investment (ROI)
- 65 • Solid Oxide Fuel Cell (SOFC)
- 66 • Steam Rankine Cycle (SRC)

- 67 • Stirling Cycle (SC)
- 68 • Stirling Engine (SE)
- 69 • Supercritical CO₂ (SCO₂)
- 70 • SuperCritical Rankine Cycle (SCRC)
- 71 • TetraThiaFulvene-TetraCyaNoQuinodimethane (TTF-TCNQ)
- 72 • ThermoElectric (TE)
- 73 • ThermoElectric Generator (TEG)
- 74 • Trilateral Flash Cycle (TFC)
- 75 • Ultra-Low Power (ULP)
- 76 • Waste Heat Recovery (WHR)
- 77 • Waste Heat to Power (WHP)
- 78 • Wearable ThermoElectric Generator (WTEG)

79 **1 Introduction.**

80 **1.1 An ecological overview.**

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

95 According to a study conducted by Vaclav Smil^[3], the world energy consumption has fol-
96 lowed a monotonically increasing trend since the beginning of the first industrial era (1840). As
97 can be noticed in Fig. 1, the speed of this growth has recently increased.* Energy consump-
98 tion is an excellent indicator for the maturity level of economics, in particular growth/recession.
99 In the first period of industrialization, energy consumption experienced a constantly increasing
100 superlinear trend. At a global scale, when the period of post-industrialization began, economic
101 growth started to stabilize and ultimately decrease, and the associated energy consumption fol-
102 lowed a fairly similar trend. CO₂ emissions are also directly correlated with economic growth.^[4]
103 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).

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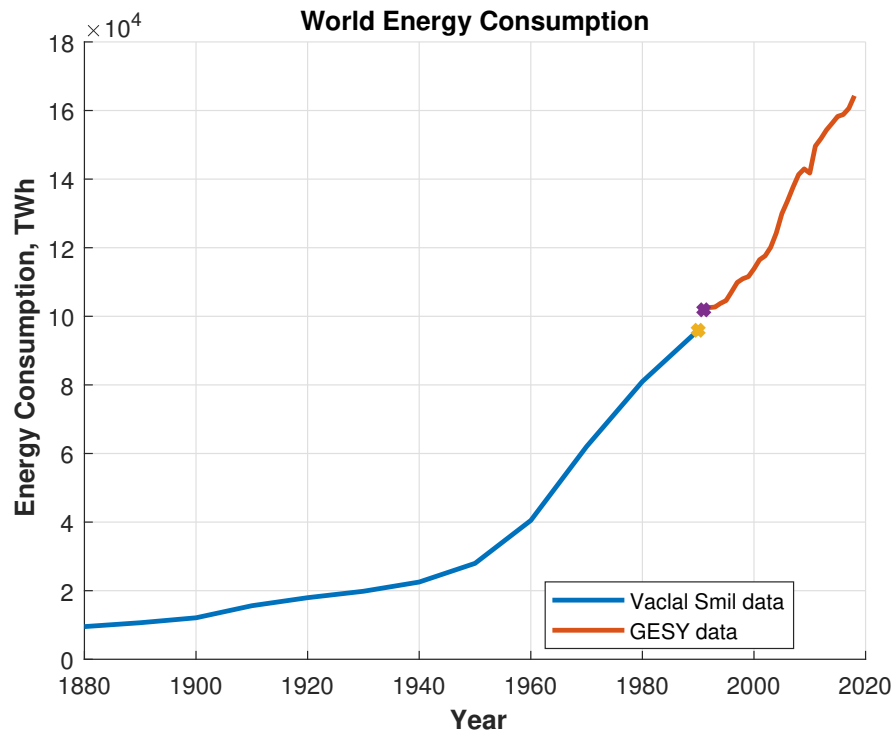


Fig. 1 Global energy consumption trend during the last 140 years. The energy sources that have been taken into account are: coal, crude oil, natural gas, hydroelectricity, nuclear electricity and biofuels for data until 1990. The data provided by the Global Energy Statistical Yearbook (red) are more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

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

110 The over-exploitation of energy sources may result in criticalities, at the political, social and
111 logistic level. It is therefore of fundamental importance to increase energy efficiency at the
112 scavenging/harvesting/transformation level. [4] Regarding the operation of industrial and power
113 plants, dilemmas arise about how to increase efficiency, how to better convert energy between
114 its forms, and how to utilize waste heat arising from thermodynamic inefficiencies (for example
115 due to friction, thermal dispersion, electromagnetic induction, etc.) or practical needs. The

116 creation of a common approach with a new attitude towards our fragile natural environment
117 is required. Alongside an increase in the consumption of primary energy, the amount of waste
118 heat increases, therefore representing a greater economic and ecological potential for utiliza-
119 tion. Although waste heat may be exploited, ideally it should be avoided: this is done through
120 the energy optimization of processes by needs-based controls, process operation and design, im-
121 proved insulation, the use of highly efficient electric drive systems and a change towards more
122 energy efficient production methods. However, even after energy optimization, significant po-
123 tential remains.^[6] Enormous amounts of waste heat injected into the environment also have the
124 side effect of locally increasing the atmospheric temperature, especially in urban environments,
125 slightly moving solution equilibria of several gaseous species. Focusing on the main GreenHouse
126 Gases (GHG) and listing them in order of importance, according to the Intergovernmental Panel
127 on Climate Change (IPCC)^{[7][8]}, they are:

- 128 • **Water Vapour** is the major contributor of all since it provokes from 30 to 70% of the overall
129 greenhouse effect^{[9][10]}. The reason for its potential resides in the large amount of this
130 chemical species in the atmosphere, enabling a positive feedback loop;
- 131 • **Carbon Dioxide** is the principal gas monitored because, even if it absorbs less heat per
132 molecule than others, it is more abundant and has a longer lifetime in air (thousands of
133 years with respect to the decades of methane). Furthermore, it plays an important role
134 in regulating the pH of the oceans, since these represent the main CO₂ reserve, and its
135 increase provokes acidification. Another positive feedback effect can be found here: a
136 temperature increase leads the oceans to release CO₂ into the atmosphere because of the
137 decrease in solubility;
- 138 • **Methane**: the impact of this gas on the greenhouse effect is 60 times that of CO₂ and a
139 monotonic increase in the last decades has been registered. However, its level and lifetime
140 are low enough to keep its contribution under control;
- 141 • **Nitrous Oxide**: its capability to absorb heat is 300 times that of CO₂ and around 40% of

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142 total N₂O emissions are caused by human activity. Moreover, its lifetime in atmosphere is
143 over 110 years making it one of the most persistent GHG;

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

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

$$Q = c m \Delta T \quad (1)$$

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

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

163 • **Thermo-economic analysis:** this aspect takes into account the Return on Investment
164 (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/enthalpy 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%

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

199 **1.3 Review outline.**

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

211 **2 Current technologies**

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

223 **2.1 Thermodynamic machines**

224 **2.1.1 Brayton Cycle**

225 The BC is characterized by a process in which air is compressed isentropically by a compressor,
226 then it receives heat from exhaust gases at constant pressure and finally it expands isentropically
227 in a turbine to generate electrical power. At this point, the air is discharged back to atmosphere
228 and the process is repeated. BC represents an optimal choice for WHR systems working at mild
229 temperatures in the industrial sector. This approach has been explored in the 1980s to convert
230 waste heat from adiabatic engines, enabling a reduction of running costs on one side and a
231 reasonable additional capital investment on the other. Recently, Zhang *et al.* (2015), proposed
232 a BC WHR system for the blast furnace slag in iron and steel industry.^[21] Song *et al.* (2013)
233 integrated a BC WHR system into a Diesel engine, connecting the turbocharger compressor with
234 the compressor that operates on the BC. Results showed that the fuel economy of the Diesel
235 engine can be improved by 2.6 % at fast rotation regimes and 4.6 % at lower regimes, under full
236 load.^[22] Galindo *et al.* (2015) investigated WHR for internal combustion engine exhaust gases

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237 using a BC machine.^[23] Gequn *et al.* (2015) proposed a CO₂ based BC to recover the engine
238 exhaust heat and compared its performances with an air-based BC. If compared to a BC based
239 on air, the results have shown that CO₂ cycle provides better results, including net output power,
240 thermal efficiency and recovery efficiency.^[24]

241 2.1.2 Stirling Cycle

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

255 2.1.3 Organic Rankine Cycle

256 Based on Rankine Cycle (RC), ORC are steam-like systems that use organic working fluids in-
257 stead of water, allowing to harvest waste heat at temperatures up to 300 °C.^[27] In ORC ma-
258 chines hydrocarbons, siloxanes, refrigerants and CO₂, can be exploited instead of water, thanks
259 to their advantageous properties in low temperature applications: lower boiling and critical
260 points, lower specific volumes, as well as lower viscosities, higher vapour pressures, and higher
261 molecular masses with respect to water-based fluids.^[27] Furthermore, ORCs are very much ap-
262 preciated in current research for the availability and the simplicity of their components and for

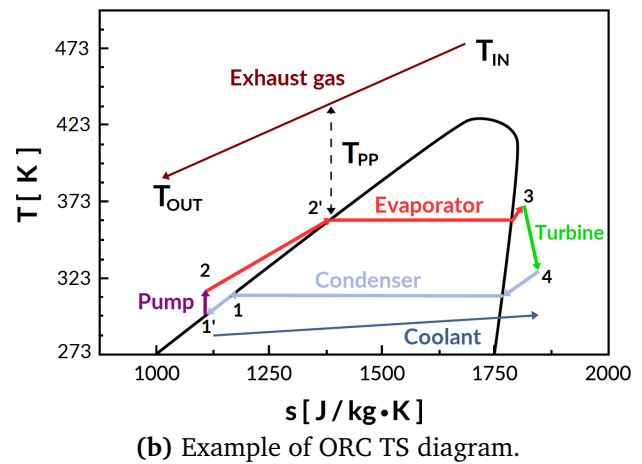
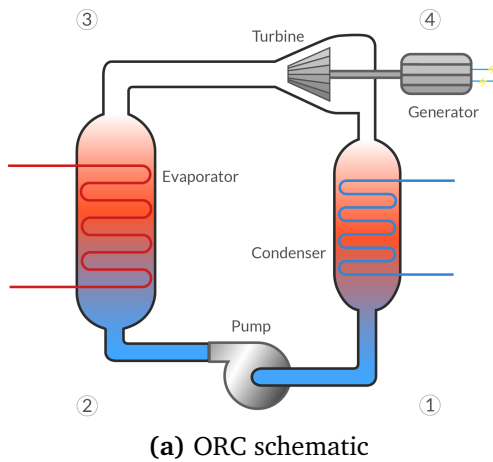


Fig. 2 Fig. 2a represents a typical schematic of an ORC system where all the components and thermodynamic transformations are shown. Fig. 2b represents an example of TS diagram using R245fa as organic working fluid.

263 the low flammability, corrosion and toxicity of working fluids. Nowadays, several ORC-based
 264 plants are installed in different countries (Italy, Austria, Germany, the Netherlands, Sweden,
 265 U.S.A., Canada, etc.) and the number of plants is still growing. The adaptability and the scala-
 266 bility of this technology permit to generate power from different heat sources (from industrial to
 267 domestic applications), selecting the dimension of the components and matching them with the
 268 choice of the working fluid. In recent years, this technology has been widely employed also in the
 269 transportation sector.^[27] The working principle of ORC is shown in Fig. 2a and its temperature-
 270 entropy (TS) diagram in Fig. 2b: a pump pressurizes the working fluid in liquid form (from
 271 point 1 to point 2); heat is then moved from the heat source to the refrigerant (working fluid)
 272 through a super-heater and an evaporator, where the organic fluid gets vaporized (from point 2
 273 to point 3); then, the high pressure working fluid flows into an expansion turbine, connected to
 274 the load (electrical power generator) (from point 3 to point 4); at the end, the cooling source
 275 controls the organic fluid returning back into liquid form in the condenser (from point 4 to
 276 point 1). There are many factors that can affect the ORCs' performances. In case the available
 277 energy is small and the available source is low-grade, to safeguard the overall performance of
 278 ORCs, attention is given to expanders (centrifugal or axial-flow turbines, allowing the expan-
 279 sion of the high-pressure gas) since they play a key role.^[1] Bademlioglu et al. (2018) provide

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280 a statistical analysis on system efficiency, using the Taguchi method.^[28] In an ORC system, the
281 main parameters affecting the design are: choice of the working fluid, pinch point, superheating
282 temperature, evaporator and condenser temperature, heat exchanger effectiveness, pump and
283 turbine efficiency, installation and running costs.

284 2.1.4 Kalina Cycle

285 The KC is an absorption-based power generation cycle, based on RC. The working fluid enabling
286 KC systems is a mixture of ammonia and water, in order to increase the recovery efficiency.
287 Condensed water-ammonia mixture is compressed isentropically, then it is heated at constant
288 pressure while it evaporates (first the ammonia, then the water), subsequently it is isentropi-
289 cally expanded into a turbine, and finally condensed (first the water and then the ammonia) at
290 constant pressure releasing heat. The operating temperature lies between and 90 and 500 °C .
291 With respect to ORC and supercritical cycles, KC shows superior performances. Since the tem-
292 perature difference between the working fluid and the heat source is reduced, reversibility is
293 increased and dissipation limited. With respect to RC, where a considerable amount of heat
294 is lost during the isothermal vaporization of water to steam, the binary mixture in the Kalina
295 cycle vaporizes non-isothermally, improving the efficiency of the cycle.^[29] Moreover, KC has one
296 more degree of freedom compared to RC, since it is possible to act on: the NH₃:H₂O ratio in the
297 working fluid and the system pressure levels. In fact, using a mixture as working fluid permits to
298 manipulate the pressure in the system by varying the composition. In this way, the thermal per-
299 formances are maximized.^[30] At given cooling conditions the pressure in the condenser can be
300 reduced by diminishing the ammonia concentration. Increasing the ammonia concentration may
301 raise the evaporation pressure.^[29] While KC allows a higher thermodynamic efficiency, the split
302 ammonia and water streams add complexity and may require an additional pumping system.
303 For this reason, plant operators and developers have different opinions about the potential of KC
304 to overcome Rankine-type power plant performance.^[31] Another relevant feature of NH₃:H₂O
305 mixtures is the extremely low amount of oxygen dissolved in the fluid, that severely reduces

306 oxidation likelihood and running costs.^[1] This process allows for flexibility in choosing boiling
307 points which can compensate for temperature fluctuations in the heat flow. Nevertheless, it is
308 a technically complex system so it is much more capital intensive and far less tested than ORC
309 modules. In the same range of temperatures it comes out that ORCs are 15 – 25 % less effi-
310 cient than KCs, with the tangible outcome that power plants featuring hot fluid below 150 °C
311 are increasingly based on this new technology.^[27] Several specific applications have produced
312 adaptations of KC systems, with more than 30 solutions which have been introduced so far. For
313 example, in cement industry, superheated NH₃:H₂O vapor is generated harvesting low-grade
314 heat; it is then expanded in a turbine, condensed in regenerative heat exchangers, diluted and
315 fed into a low-pressure condenser, and finally injected into the high-pressure condenser before
316 reaching again the vapor generators.^[1]

317 2.1.5 Carbon Dioxide Trans-Critical Cycle

318 As above mentioned, to recover or convert waste heat by means of thermal machines, organic
319 and natural fluids are often used. Worth noting, CDTCC technology, being based on CO₂, pro-
320 vides non-toxic, non-flammable, non-corrosive operation. CO₂ reaches the supercritical state at
321 7.38 MPa and 31.1 °C and is therefore widely applied to low-grade heat recovery systems.^[32]
322 By intelligent design of a CDTCC system, heat is rejected below the critical point and absorbed
323 above, having therefore a working fluid in the superheated state under supercritical pressures,
324 resulting in maximized performances.^[33] The working principle is the same described in the
325 ORC, but in this case, CO₂ is isentropically compressed, heated at constant pressure, isentropi-
326 cally expanded and finally condensed releasing heat at constant pressure. Cayer *et al.* (2009)
327 applied four different methodologies on a CDTCC power cycle with a low-grade energy heat
328 source and performed a parametric optimization.^[34] Li *et al.* (2017) theoretically compared a
329 CDTCC power cycle and a R245fa ORC, operating on a low-grade heat reservoir and concluded
330 that the exergy efficiency would benefit from using a recuperator.^[32,35]

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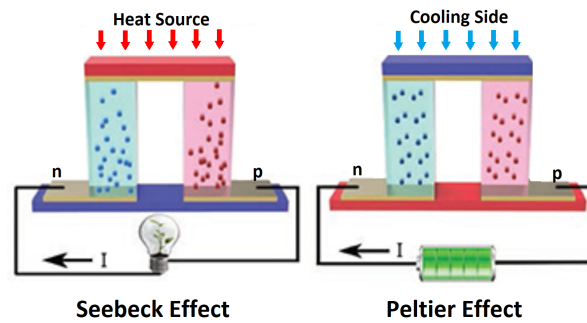
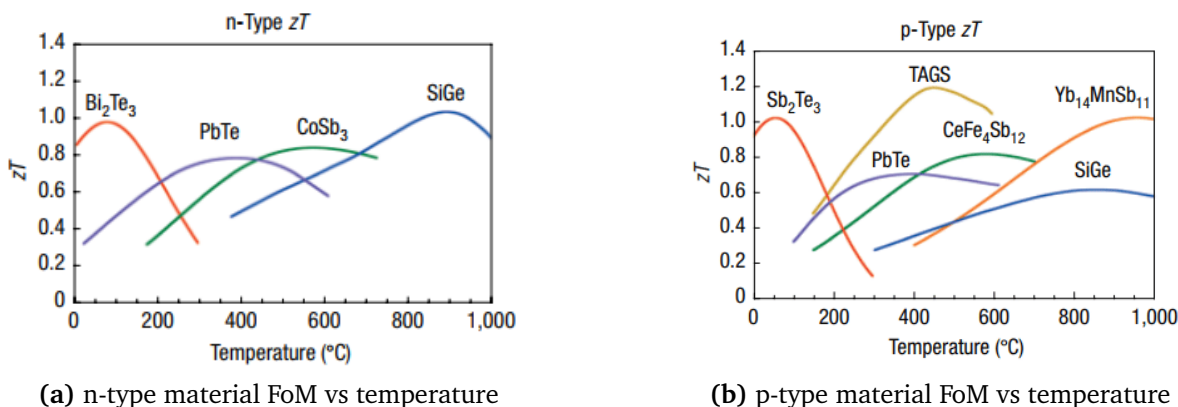


Fig. 3 Thermoelectric effects: in the left figure the typical representation of a thermocouple based on Seebeck effect is reported whereas in the right one, the Peltier effect is represented.

331 2.2 Thermoelectric systems

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

343 In general, the materials can be divided in three categories depending on the temperature
344 of operation: low (below $250\text{ }^{\circ}\text{C}$), medium ($250\text{-}600\text{ }^{\circ}\text{C}$) and high (above $600\text{ }^{\circ}\text{C}$) working
345 temperature. Since the first devices until nowadays, Bismuth is the most widely used material
346 for low-temperature applications. The Seebeck coefficients is deeply dependet on the effective
347 mass and mobility of the carriers^[36]. For this reason, antimony-telluride Sb_2Te_3 or its alloys
348 are used for p-type composition instead of bismuth-telluride, since their higher carrier mobility.
349 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 $T \leq 200\text{ }^{\circ}\text{C}$, Bi₂Te₃ and Sb₂Te₃ show the highest zT value. Reproduced with permission.^[36] Copyright 2008, Springer Nature.

350 hence, finely tune the material specific Figure of Merit (FoM)[†]. Moreover, Fig. 4 shows why
 351 both Bi₂Te₃ and Sb₂Te₃ are, at LT, the most suitable materials to be used, since they feature the
 352 highest FoM in this temperature range.

353 Recent studies by Pacific Northwest National Laboratory considered some well known in-
 354 dustrial activities, such as aluminum smelting, glass manufacturing, and cement production,
 355 and concluded that small internal combustion engines could be profitably replaced by external
 356 combustion TE engines, vibration-free and less impacting from the acoustics point of view. TE
 357 engines can be driven using several fuels, as for example propane, butane, liquefied natural gas,
 358 bio-alcohols, and not necessarily based on fossil sources.^[37] Both United States and Japan Gov-
 359 ernments have introduced regulations to help companies introducing TE devices in trucks and
 360 cars to partially convert waste heat from the exhausts into electricity, powering steering, brakes,
 361 water pumps, turbo-chargers, etc. Although efficiency estimates depend on the degree of system
 362 integration and on driving conditions, Diesel consumption (nowadays highly diffused among de-
 363 veloped countries to enable on site power generation) could be reduced by 5 to 10 %^[37]. Several
 364 leading automotive manufactures such as Volvo, Volkswagen, BMW, and Ford are introducing
 365 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.

2. CURRENT TECHNOLOGIES

366 thermal engine overall efficiency by using TE generators. Hsu *et al.* invented a WHR system for
367 automotive exhaust heat recovery composed by 24 TE modules able to provide approximately
368 12 W (electrical) with a ΔT of 30 °C [27]. Sano *et al.* developed a very efficient TE module (15
369 % efficiency) [27]. Furthermore, Solar Thermoelectric Generators (STEGs) have been developed
370 efficiently coupling thermal solar collectors with TE devices, since the absorbed heat is conveyed
371 on the TE devices by means of a diathermal fluid.

372 2.3 Pyroelectric systems

373 Another effect that can be exploited in energy harvesting, is pyroelectricity, through the so called
374 pyroelectric (PE) effect. Unlike thermoelectricity, where a stable (stationary) temperature gradi-
375 ent is needed, this effect allows to displace electrical charges from temporal temperature changes
376 across a suitable material or device. PE allows to avoid the main issue of Thermoelectric Gener-
377 ators (TEGs), i.e. the need of huge heat flows in order to sustain a large temperature gradient.
378 This observation has brought attention on PE devices which promise a better efficiency and ease
379 in installation. The main parameter defining the PE performances is the pyroelectric coefficient
380 [$\text{C m}^{-2}\text{K}^{-1}$], described as the change in the spontaneous polarization vector with respect to
381 temperature. Several kinds of PE materials have been studied trying to find the best compro-
382 mise to enhance efficiency in the realization of PE generators (PEGs). Lead zirconate titanate
383 (Pb,ZrTiO_3 (PZT) or barium titanate BaTiO_3 (BT), feature the highest known PE coefficients
384 (-268 and $-200 \mu\text{C m}^{-2}\text{K}^{-1}$, respectively). A collection of information about the most popular
385 PE materials has recently been produced [38]. In the work developed by Sebald *et al.* (2009) a
386 comparison between the performances of TEGs and a PEG is reported [39]. It is shown that lin-
387 ear materials, i.e. those having the dielectric constant which increases linearly with the applied
388 electric field, are able to produce just few $\mu\text{W cm}^{-3}$ for temperature variations of 20 °C with
389 a frequency of 10^{-2} Hz. However, using nonlinear materials, the performance can be strongly
390 increased by adopting particular thermodynamic path cycles like:

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

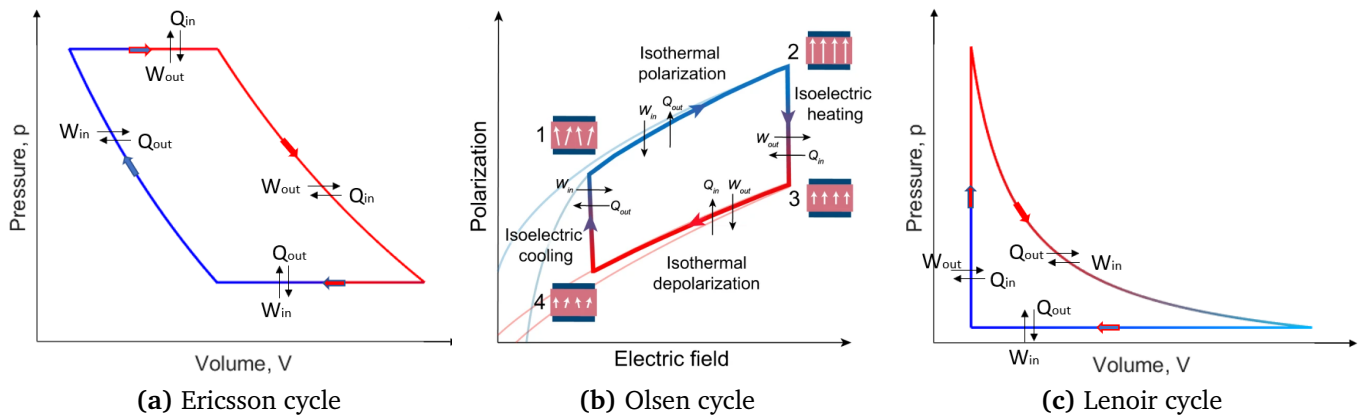


Fig. 5 The 5a represents the typical trend of an Ericsson cycle. The 5b image is representing the typical Olsen cycle where the polarization is represented as a function of electric field E .^[40] Finally, the graph 5c represents the Lenoir cycle. The colourmap indicates the temperature variation.

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

- 394 • **Olsen** cycle, formed by two isoelectric processes and two isothermal ones. Several experi-
 395 ments have been conducted with different materials under different crystalline forms (e.g.
 396 single crystal and thin film).^[43–45] It is represented in Fig. 5b;
- 397 • **Lenoir** cycle, It is a formed by 3 transitions: isochoric heat injection, isentropic expansion
 398 and isobaric heat rejection. Mohammadi *et al.* (2012) showed that this cycle in comparison
 399 to the Ericsson one results in a much bigger amount of harvested energy in the latter.^[46]
 400 It is represented in Fig. 5c.

401 In the work of Sebald *et al.* (2009) the results obtained testing different materials are reported,
 402 and the increase of power output is quite evident, moving from a few $\mu\text{W cm}^{-3}$ to hundreds of
 403 $\mu\text{W cm}^{-3}$ ^[39]. From the analysis of heat exchanged and other properties of TE and PE effects, it
 404 turns out that even though the power generated by PEGs is low, their efficiency is much higher
 405 than that of TEGs. A complete analysis of PE efficiency for each of the cycles here introduced can
 406 be found in the work of Batra *et al.* (2013)^[47]. A more detailed explanation of the phenomena
 407 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 CO₂ (SCO₂) 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 CO₂ Brayton Cycle

The SCO₂ BC is a standard thermodynamic cycle operating with CO₂ 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, CO₂ 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 m³ of installed plant, one order of magnitude below steam/gas turbines. SCO₂ 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

3. EMERGING TECHNOLOGIES

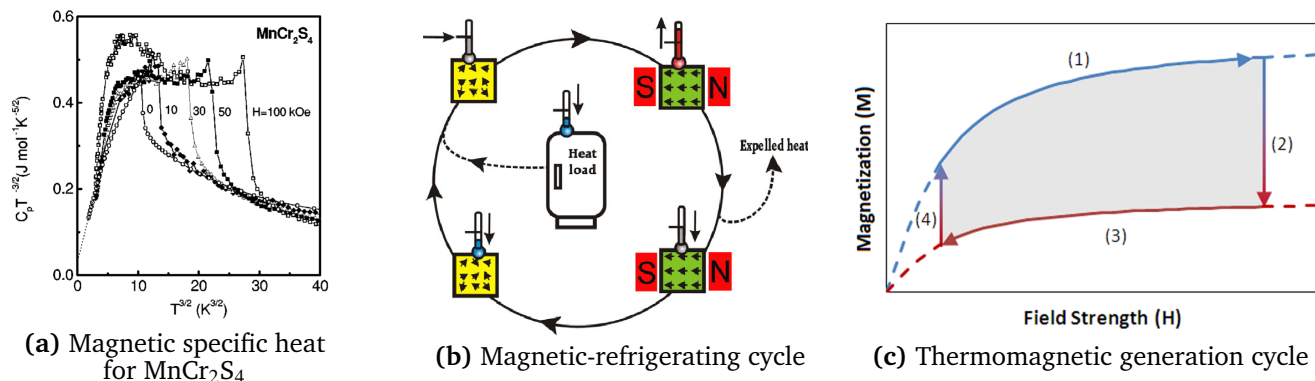


Fig. 6 Fig. 6a represents the specific magnetic heat for a ferromagnetic material, in this case MnCr_2S_4 crystals. Reproduced under the terms of the RNP/20/APR/024834 license.^[51] Copyright 2020, American Physical Society. 6b shows the magnetic-refrigerating cycle related to magnetocaloric materials 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.

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

469 3.4 Thermomagnetic Hydrodynamic machines

470 Magnetic colloids, such as FerroFluids (FFs), are nano-materials that present high magnetic sus-
471 ceptibility (some orders of magnitude higher than other non-magnetic natural substances).^[55]
472 In fact, when no external magnetic field is present, magnetic moments are randomly oriented
473 inside the carrier fluid, and the resulting net magnetization is equal to zero. Otherwise, if the ex-

474 ternal magnetic field is present, the dipoles align along the direction of the field, and a non-zero
475 net magnetization appears. FFs can be used to harvest energy, giving the possibility to imple-
476 ment a low-power micro-generator, especially suitable for electronics where battery replacement
477 has higher costs and is quite difficult to be performed.

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

485 In literature several methods to harvest energy using a FF are described, in particular from
486 a thermal gradient: ^[56] describes a way to produce electrical power by exploiting the FF motion
487 activated by convection currents generated by a thermal gradient. Furthermore, it is possible to
488 generate solitonic density waves inside a closed loop system wrapped with copper wire coils, in
489 order to extract electromagnetic forces and electric power, giving birth to the first generation of
490 colloidal energy harvesters. ^[57] In all the cases where the gravitational field is parallel to both the
491 thermal gradient and the external magnetic field, it is possible to exploit the Benard-Marangoni
492 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 CO₂ 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

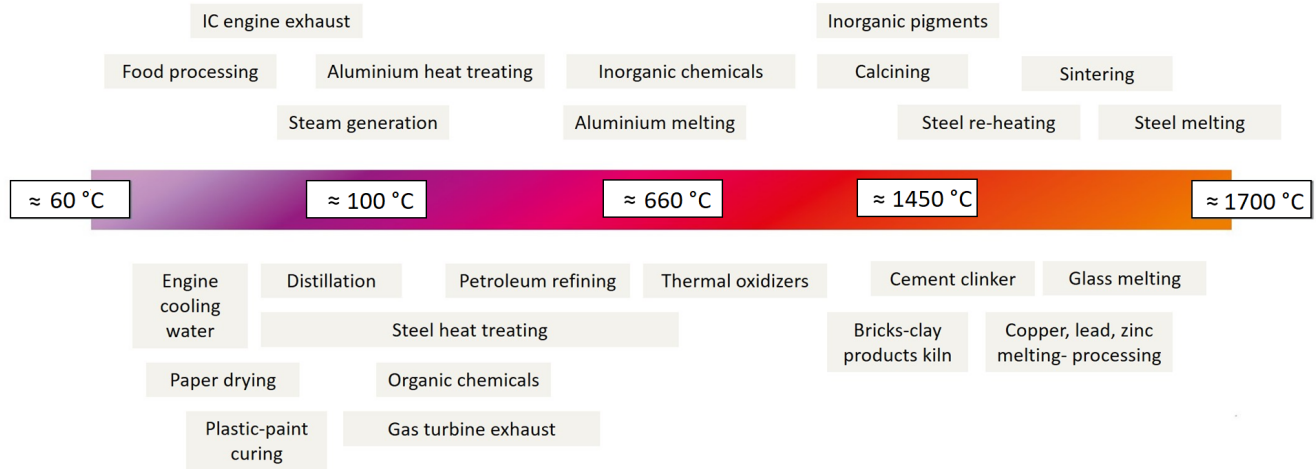


Fig. 7 Temperatures range for different industrial heating processes.^[5]

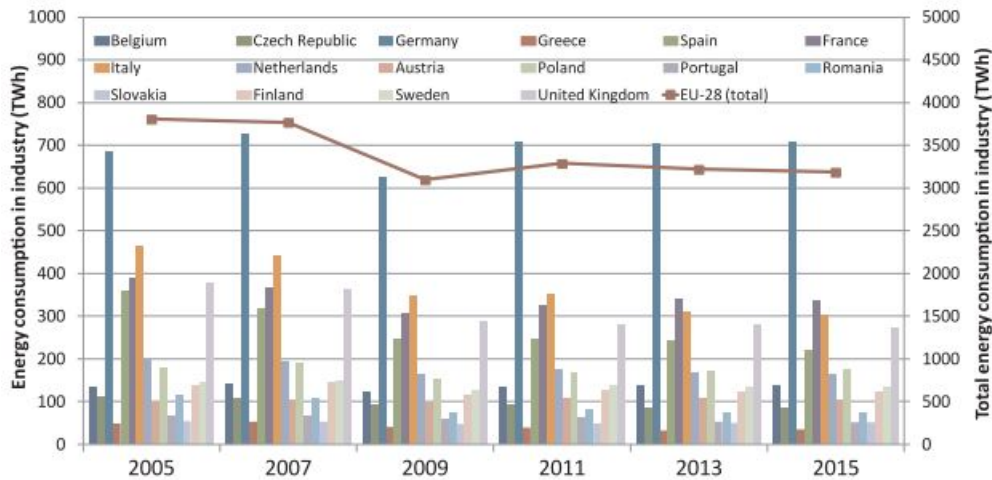


Fig. 8 Waste heat potential in each EU country per year in all industries. Reproduced under the terms of the 4811241236352 license.^[61] Copyright 2020, Elsevier.

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

520 4.2 Technical potential of the waste heat from industrial activities

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

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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

526 mineral transformation industries in U.S.A. are wasting 20 – 50 % of the energy used. McKenna
527 and Norman (2010) conclude that the recovery potential for energy intensive industries in the UK
528 is around 10 % of the total heat quota.^[62] Waste heat potential in the EU has been estimated to
529 lie above 350 TWh/year, the greatest part falling in the 100 and 200 °C range. Waste heat below
530 100 °C represents a marginal portion, while within the 200 and 500 °C range more important
531 quantities are found.^[61] This is an important amount of energy compared to the 3,218 TWh
532 energy consumption of 2016.^[61] Papapetrou *et al.* (2018) developed a statistics related to the
533 waste heat potential in percentages per industry sector for all the former countries belonging to
534 EU28.^[61] The results are reported in Table 1.

535 4.3 Technology overview

536 4.3.1 Thermodynamic machines

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

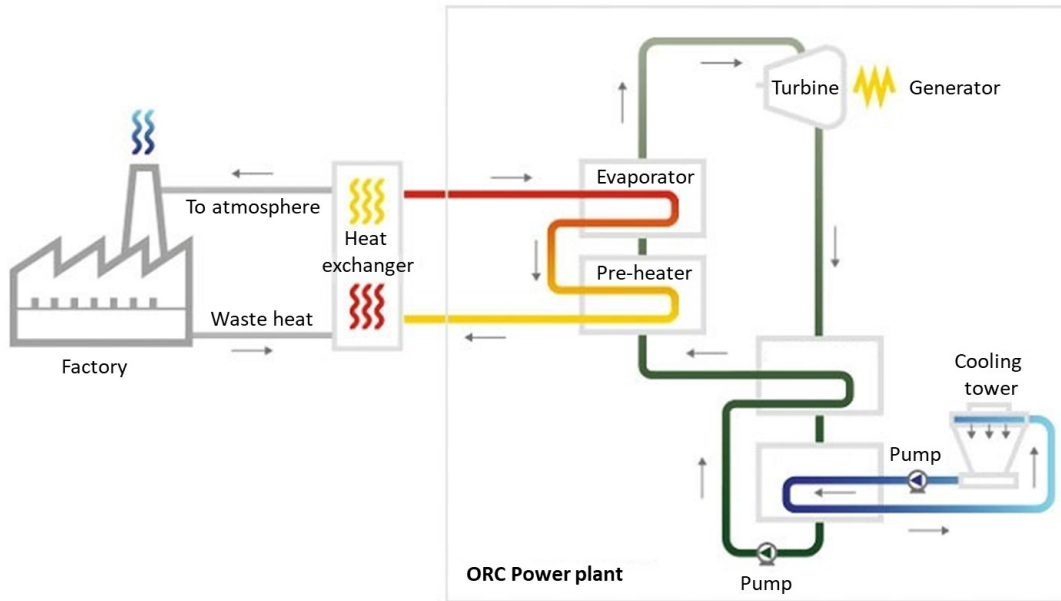


Fig. 9 Schematic of ORC installation in an industrial plant.^[63]

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

553 KCs can recover industrial waste heat in the range 80 to 400 °C for power generation. Ex-
 554 isting industrial WHR applications include: Sumitomo plant in Japan with an installed plant
 555 producing 3.5 MW since 1999; Husavik, Iceland plant which converts 2.0 MW since 2000; Fuji
 556 Oil plant in Japan converting 4.0 MW since 2005; DG KHAN plant in Pakistan converting 8.6 MW
 557 since 2013; Star Cement plant in Dubai producing 4.75 MW since 2013. KCs are limited in their

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558 industrial applications for some technical issues that have not been solved, yet, in particular the
559 need for a fine tuning of the boiler evaporation ratio and the early condensation of $\text{NH}_3\text{-H}_2\text{O}$
560 mixture. [1]

561 Solid Oxide Fuel Cell (SOFC) is considered an emerging technology for both small and large
562 power plants for high efficiency power generation with low emissions. A comparative analysis
563 in terms of energy and exergy has been conducted, for employing ORC and KC for waste heat
564 recovery from hybrid SOFC/GT systems. The results show a good motivation for employing ORC
565 or KC for WHR to increase the global energy conversion efficiency. The results indicate the su-
566 periority of ORC over KC. [64] A comparison of performances between KC and transcritical ORC
567 for WHR in different internal combustion engine working conditions. Compared to KC, the tran-
568 scritical ORC shows evident advantages on the overall thermodynamic efficiency, low operation
569 pressure and simple components configuration with exhaust temperature from the engine over
570 $220\text{ }^\circ\text{C}$. The optimal thermal performance of the transcritical ORC is in the range $295\text{-}345\text{ }^\circ\text{C}$.
571 Nevertheless, moving over or under the optimal temperature drop the performances decrease
572 considerably. Moreover, the extremely high expansion ratio of the turbine requires a complex
573 multi-stage design and large dimensions. [65] Another comparison between the thermodynamic
574 performances of KC and ORC has been conducted for the case of heat recovery from two Diesel
575 engines, each one with an electrical power of 8900 kWe. Supposing a mean temperature differ-
576 ence in the heat recovery exchanger of $50\text{ }^\circ\text{C}$, a net electric power of 1615 kW and of 1603 kW
577 can be generated, respectively, for KC and ORC. Although the output levels are almost equal,
578 KC requires a much higher maximum pressure in order to obtain high performances. Then, at
579 least for low power level and MT and HT thermal sources, KC appears to be unjustified because
580 the increase in performances is very small (with respect to a properly optimized ORC) and must
581 be obtained with a more complex plant scheme, larger surface heat exchangers and particular
582 plants featuring pressure and corrosion resistance. [66]

583 In the last decade, the development of innovative thermodynamic cycles has been funda-
584 mental for the efficient utilization of low temperature heat sources such as solar, geothermal

585 and waste heat sources and many researchers started to explore these technologies. Padilla *et al.*
586 (2010) analysed a hybrid power/cooling cycle, which combines RC and absorption refrigeration
587 cycles, using ammonia-water mixture and generating power and cooling at the same time. Also
588 known as the Goswami Cycle, it can be employed as a bottoming cycle using waste heat from
589 conventional power cycle or as independent cycle using solar or geothermal energy. The results
590 show that with a heat source temperature between 90-170 °C and the absorber temperature
591 of 30 °C, the maximum First Law efficiency (ratio between the net output power and the heat
592 absorbed from the high temperature source to produce it) and exergy efficiency are estimated to
593 be 20% and 72%, respectively.^[67]

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

598 4.3.2 Thermoelectric devices

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

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611 This is composed of one TE module hold by two copper layers with 4 heat pipes generating the
612 temperature difference between the two TEG sides^[70]. Another application of TEG modules is
613 in support of the Industrial Wireless Sensor Networks (IWSNs), clusters of wireless sensor nodes
614 in industrial plants and commercial areas. They consist of a high number of sensor nodes, in-
615 cluding sensor units and control electronics, communication and power supply. Most of these
616 are powered by means of batteries having strong limitation in terms of energy because of the
617 constrained node and battery size. Therefore, several researchers explore the possibility of cou-
618 pling IWSNs with TEGs in order to harvest energy and extend batteries lifetime, achieving higher
619 power densities with respect to other energy harvesters. It has been concluded that, with 0.6 m/s
620 of air flow on the TEGs and without using any heat sink, the hot side being at 50 °C and the
621 cold one at 20 °C, the output power is around 80 μ W. Dalola *et al.* (2009) used a TE component
622 to supply an autonomous sensing node for T measurement.^[71] Bonin *et al.* (2013) produced
623 and characterized small TE generators used to power systems for environmental monitoring, in
624 the order of 10 mW for a temperature difference of 10 °C.^[72] In another application domain,
625 52 % of Australian households hot water heaters are powered by using natural gas and Liqui-
626 fied Petroleum Gas (LPG) systems. By exploiting the thermal gradient generated between hot
627 exhaust gas exiting and cold water from ducts, it would be possible to generate power by means
628 of TEGs. Through the testing conducted, a power generation unit including 60 TE cells would
629 be able to produce more than 40 W and more than 20 W in case the hot water is around boiling
630 temperature and 80 °C, respectively. In the latter case, the efficiency of the system is estimated
631 to fall in the range 0.37 % to 1.03 %.^[73]

632 Furthermore, some hybrid concept and devices have been analysed. Gholamian *et al.* (2018)
633 focused on enhancing the performances of a geothermal-based ORC and proposed two novel sys-
634 tems in which, in the first case, part of the waste heat is recovered employing a TEG for power
635 generation while in the second for hydrogen production (by means of proton exchange mem-
636 brane electrolyzer). Results indicated that the proposed system has exergy efficiencies higher
637 than that of the basic ORC by 21.9% and 12.7%, respectively. They also reveal that the specific

638 product cost for the proposed solutions is lower than that for the basic ORC, despite an higher
639 total cost rate.^[74] Zare *et al.* (2017) studied the possibility of employing TEG to recover the
640 waste heat from a KC and the results revealed an improvement of around 7.3 % of the net out-
641 put power and higher energy and exergy efficiencies. Furthermore, they evaluated economically
642 the integration of TEG with the KC indicating a modest profitability.^[75]

643 4.3.3 Novel approaches

644 Recently, innovative method for low-grade waste heat recovery based on nanogenerators have
645 been deeply investigated and, even though a large margin for improvements is still present, some
646 interesting results have been reached. To be mentioned is the work of Raouadi *et al.*^[76] where
647 an hybridized pyro-vortex device, realized in polyvinylidene fluoride (PVDF), has been realized,
648 with an area of 2 cm². The idea behind this work is to exploit the energy of the wind to realize an
649 inexpensive and efficient harvester providing an uninterrupted energy output. In particular, the
650 vortexes generated by this latter give rise to two conversion mechanism: molecular transport,
651 proportional to the gradients of the averaged velocity of the wind and heat fluxes, and convec-
652 tive transport, who gives rise to turbulent stresses caused by the momentum transfer produced
653 by the velocity fluctuations. In fact, this device allow to produce a stable output current reaching
654 a maximum power density of 2.82 $\mu\text{W}/\text{cm}^2$.

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

663 A combination of pyroelectric and triboelectric hybrid energy harvester has been also pro-

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

673 Two innovative works propose a liquid-state low-grade waste heat harvester. The idea is to
674 combine solid and liquid properties, realizing a stable suspension of nanoparticles in a carrier
675 fluid, and move this mixture by means of a combination of thermal and magnetic flux gradient.
676 This thermomagnetic motion will allow the nanoparticles to crawl on the walls of the container,
677 provoking charge accumulation by means of triboelectric process,^[79] and to experience a tem-
678 perature variation in time, provoking pyroelectrification^[80]. At the state of the art the device has
679 been tested only in laboratory and still need some improvements to be reproduced in large scale.
680 However, the results are encouraging and the possible application are various since the device,
681 until now is proposed in two shape, i.e. toroidal or planar, and can be applied on whatever hot
682 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 CO₂ 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.

5. AUTOMOTIVE APPLICATIONS

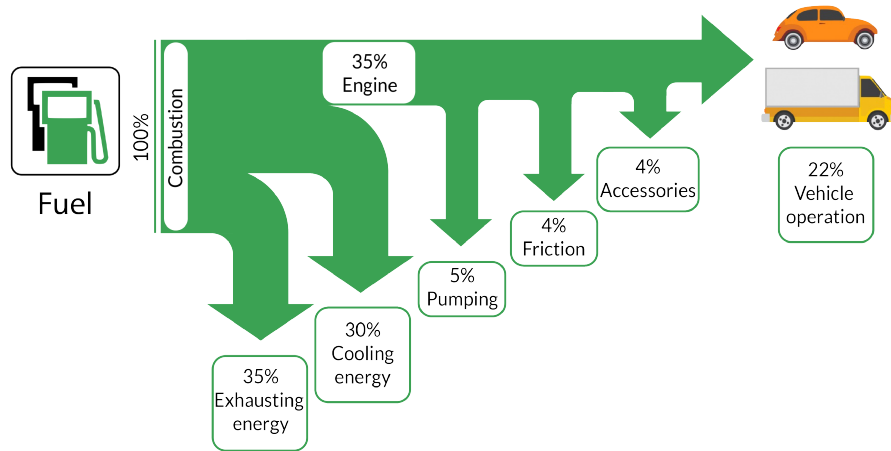


Fig. 10 A Sankey diagram showing the fuel energy utilization of an ICE.

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

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

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

724 A further important feature is thermal availability, or rather the entropy maximization, repre-

725 sending the maximum amount of work necessary to establish equilibrium in the system^[89]. This
726 concept is closely related to heat grade (temperature). While HT and MT conditions are widely
727 used for practical power generation, LT sources represent today's challenge in the automotive
728 industry. LT sources are mainly localized in the cooling systems (radiator and air conditioning)
729 and in exhaust gases exiting other recovery devices.^[90]

730 5.3 Technological Overview

731 From a historical point of view, the first approach adopted in WHR for the automotive field is
732 the Mechanical Turbo-Compounding (MTC). This technique employs a turbine to extract energy
733 from HT/MT thermal energy (from 400 to 600 °C^[91]) using the combustion gas streams. At
734 present, Detroit Diesel, Iveco, Volvo and Scania truck manufacturers produce engines that make
735 use of this recovery technique. MTC technology is essentially based on the concept of additional
736 heat by a second exhaust turbine from a turbocharger: instead of ejecting the excess of energy
737 via the exhaust pipe, it is possible to extract additional heat by using a second exhaust turbine.
738 The rotational motion passes through a gear system and a hydraulic coupling, boosting the
739 torque available on the crankshaft. This permits to have extra driving force without additional
740 fuel expenditure. Several studies show that MTC improves the thermal efficiency from 3 % to 5
741 %.^[92] The main disadvantage of this technology is that MTC design expects the interaction of the
742 recovery system with the engine, generating an exhaust back-pressure. This makes it suitable
743 only for HDV industry. The ICE cooling system is the most promising area of investigation to
744 exploit LT recovery.^[93] The low mass flow rate of the working fluid can guarantee the realization
745 of smaller size recovery systems.

746 5.3.1 Organic Rankine Cycle

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

5. AUTOMOTIVE APPLICATIONS

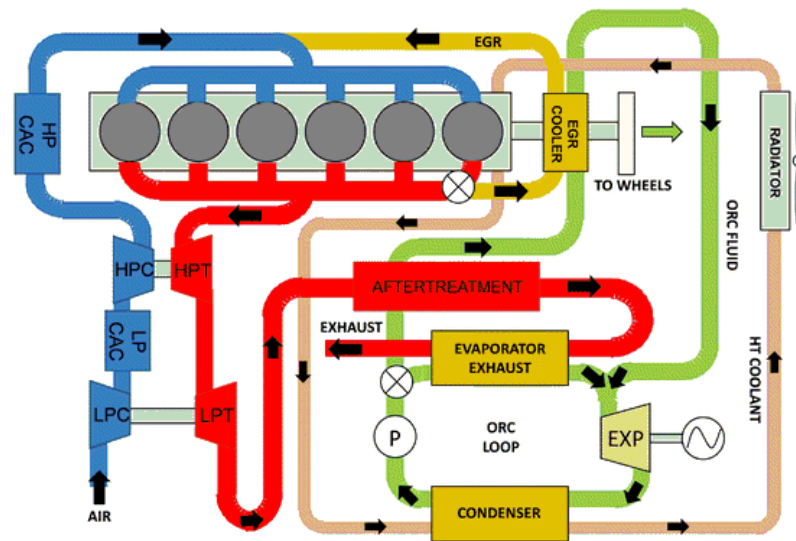


Fig. 11 Model of ORC in an automotive system. Reproduced under the terms of the Attribution 4.0 International license.^[94] Copyright 2017, Springer Nature.

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

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

767 is possible to reach higher efficiencies,^[106] but the system is heavy and cumbersome, therefore
768 economically unfavourable for automotive applications.^[91] Other approaches^[107] involve the
769 use of the heat rejected by the cooling system for the confluent cascade expansions ORC system.

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

785 5.3.2 Thermoelectric Generators

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

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

5. AUTOMOTIVE APPLICATIONS

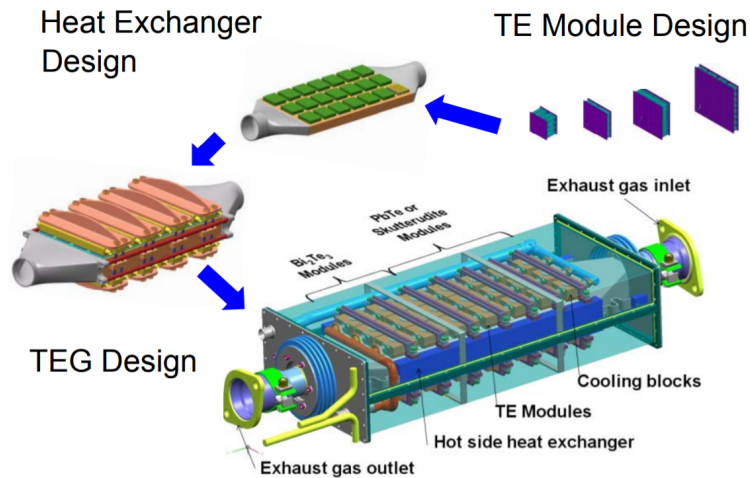


Fig. 12 Example of ETEG design.^[110]

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

805 Komatsu (Japan), Marlow (USA) and HiZ (USA) produce and commercialize TEG modules
806 using Bi₂Te₃ as active material. In particular HiZ produces several devices that work with a
807 maximum temperature of 250 °C and a ΔT of 200 °C, producing from 2 to 20 W of electrical
808 DC power. The cost of these devices can range from 18 EUR to 80 EUR per module, depending
809 on dimensions and on purpose.

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

817 An interesting experimental study^[114] shows that using six Bi₂Te₃ TEG modules on a 3,696
818 c.c. gasoline engine having hot and cold sides at 225 °C and 255 °C respectively, it is possible
819 to generate an output power of more than 40 W. In accordance with other researches^[115,116]
820 the fuel economy of a vehicle can be improved up to 2 % using LT exhaust gases.

821 A different approach for WHR is proposed by Park, Yoo and Kim (2010).^[117] As in the ORC
822 case, they recover energy from the engine coolant, substituting the radiator system with a system
823 of 72 TE modules (Bi₂Te₃ with an area of 4mm × 4mm) and 128 heat pipes. The coolant flows
824 inside a chamber where the squared modules are installed, transferring heat to the hot surface
825 of the material and reaching 95 °C. To keep the temperature of the cold side at 25 °C, a
826 standard air-cooling system has been used. Results show that it is possible to generate almost 30
827 W of electrical DC power during idle condition and almost 75 W during driving condition. This
828 approach allows to recover 0.4 % of wasted heat.

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

834 6 Wearable applications

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

848 6.1 Thermal energy harvesters

849 According to^[123] the energy requirements of an average person under 60 years are in the range
 850 of 8.8 to 17.6 MJ per day (man) and between 7.1 to 14.2 MJ per day (woman)^{††}. Therefore
 851 assuming that on average the daily energy need is about 10 MJ and the corresponding power
 852 is $\approx 120\text{ W}$, considering to radiate a large part of this energy in form of heat, a thermal source
 853 of some tens of Watts, at rest, is available^[124]. Therefore harvesting even a small part of this
 854 energy would enable powering wearables such as smartwatches, that need a few tens of mW to
 855 operate^[125]. Assuming a normal condition, that is a body temperature of $36.6\text{ }^\circ\text{C}$ ^[126] and a
 856 room temperature of $27\text{ }^\circ\text{C}$, it is possible to estimate a Carnot efficiency of approximately 3%,
 857 which makes immediately clear the constraints for the application on a human body. However,
 858 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).

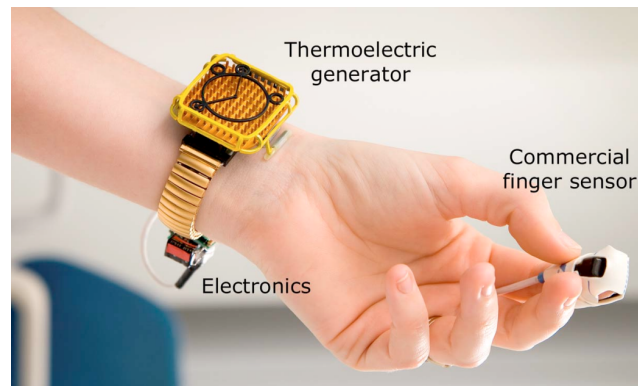


Fig. 13 Fully powered wireless pulse oximeter:^[129] on the forefinger a commercial sensor has been placed. The wristwatch TEG charge a storage capacitor able to provide 0.7 – 2 V as output voltage. A DC/DC converter to ensure stable and higher V_{oc} is mounted after the capacitor itself. A $V = 2.05$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

859 sufficient to power wearables.

860 6.1.1 Rigid and flexible thermoelectric devices

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

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

6. WEARABLE APPLICATIONS

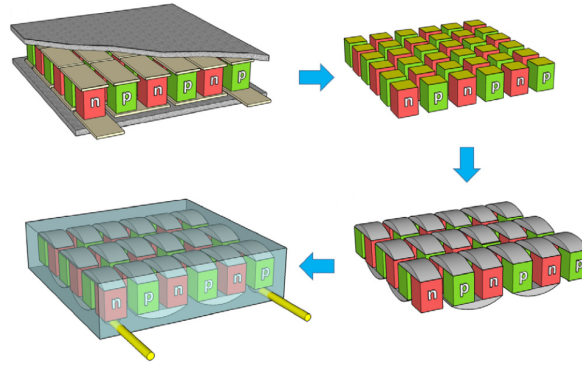
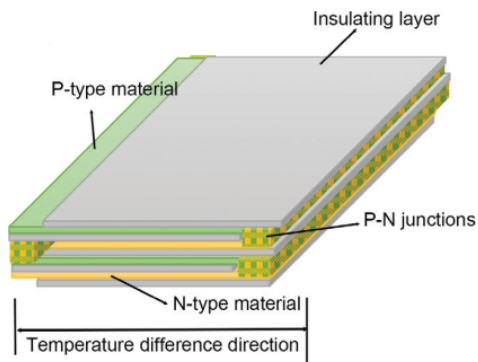


Fig. 14 Scheme of the transition from rigid to flexible device substituting the ceramic plates with liquid bendable connection. Notice that the legs are the same of the rigid device. Final step consist in an encapsulation in polydimethylsiloxane (PDMS). Reproduced with permission.^[134] Copyright 2017,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

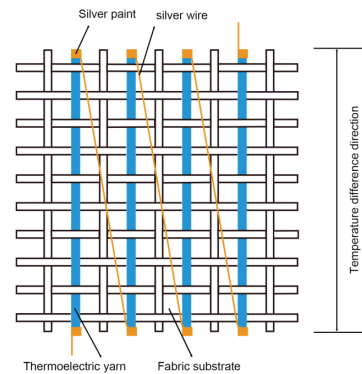
876 TEG system is able to generate up to $20 \mu\text{W}$ at RT with respect to the $3.7 \mu\text{W}$ of a 5 cm^2 piezo-
877 electric one. By properly setting the parameters, they reached $V_o = 12 \text{ mV}$ and $V_{oc} = 24 \text{ mV}$ for
878 a of $0.5 \text{ }^\circ\text{C}$, i.e. output and open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

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

891 It is important mentioning also the work proposed by Wu *et al.*^[135] (2018) that tried to look
892 for another way to integrate the harvesting system directly into the clothes' fibers. They have
893 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]

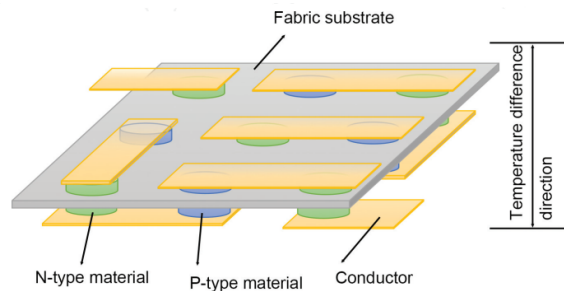


Fig. 16 Arrangement for a 3D textile thermoelectric generator proposed by Kim *et al.* in 2014. This kind of structure allow to sustain a temperature gradient along the thickness contrarily to 2D structures.^[136]

894 heat recovery) and production (fabric finishing and coating or fibers/yarns coating technologies)
 895 points of view. These can be a very good alternative to other kind of devices thanks to the ease
 896 of integration, comfort and air-permeability. Their structure is different since does not rely on
 897 a sandwich design but on a planar one. This implies that the temperature difference is applied
 898 along the length and not the thickness of the leg for stability reasons. However, they can be
 899 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>

900 6.1.2 Pyroelectric energy harvester

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

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

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

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

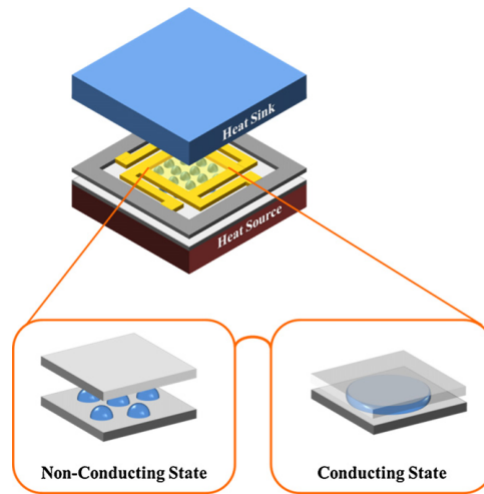


Fig. 17 Image of the Liquid-Based Thermal Interface device structure proposed by Cha *et al.* in^[143], 2012. Reproduced with permission.^[143] Copyright 2012, Elsevier.

926 established, in the thermocell a redox of ferrous/ferric chloride acid develops converts it in use-
 927 ful electric energy. Moreover, an analysis on performance versus the content of CNTs in CNCs
 928 is performed resulting in a verification of the crucial role played by CNCs. The thermogalvanic
 929 cell has shown a current density production of 1.2 A m^{-2} for a of $100 \text{ }^\circ\text{C}$. Assuming an illumi-
 930 nation of AM 1.5 G, the PVDF film generates up to 200 V of output voltage under illumination
 931 and -120 V once the illumination is removed. The importance of this device lies mainly in its
 932 versatility since it can harvest energy in difference conditions, being thus able to act as a supply
 933 24/7. The hybrid has shown a maximum output power produced of 1.86 and 0.9 mW m^{-2} for
 934 the thermogalvanic and pyroelectric components, respectively. Recently, a wearable pyroelec-
 935 tric nanogenerator based on the breathing process has been proposed in the work of H. Xue *et*
 936 *al.*^[144] where they successfully introduced a thin film of polyvinylidene fluoride (PVDF), of di-
 937 mensions $35 \times 35 \text{ mm}$ and thickness $30 \text{ }\mu\text{m}$, in a mask. Exploiting the heat released by the breath,
 938 the maximum temperature variation registered on the harvester was $12 \text{ }^\circ\text{C}$ and the maximum
 939 power extracted, with an external load of $50 \text{ M}\Omega$, reached $\approx 0.68 \text{ }\mu\text{W/cm}^2$.

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

7. CONCLUSIONS

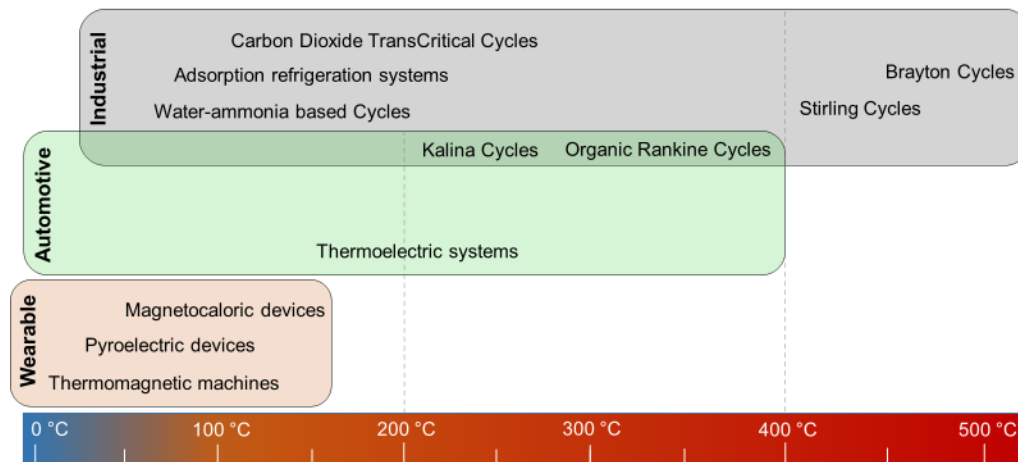


Fig. 18 Most of the technologies analysed, grouped according to their application field and optimal temperature range of operation. Note that this graphical summary is conceived only to give an immediate, qualitative glimpse on the statistics of technology application. For this reason, the reader should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

943 7 Conclusions

944 The identified technologies have been collected and sorted according to their typical application
945 and optimal temperature range in Fig. 18. A comparison in terms of efficiencies, post-installation
946 costs per kW and typical installed power output is given in Table 2. The reader should never
947 forget that closed loop thermodynamic cycles based on any specific fluid feature intrinsic instal-
948 lation costs that strongly limit their power output lower bound, while purely solid state systems
949 such as TEGs and PEGs suffer from the specular limit, toward upper bound. Once the available
950 WHP technologies have been analysed, question arises on whether they could represent a valid
951 approach to increase the quota of "green" installed power, working both in conjunction with
952 fossil fuel-based processes and renewable resources-based processes. Considering their costs per
953 kW and comparing them to photovoltaic systems (on average the cost per kW is 1.4 kEUR/kW as
954 of December 2018), two technologies are already competitive: BC and ORC. On the other side,
955 the higher production costs of wind turbines (on average 1.4 kEUR/kW as of 2017 for onshore
956 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 ($T_{Hot} = 20-200\text{ }^{\circ}\text{C}$)	0.40 ^a	0.13	0.10 ^d	0.15 ^f	0.12 ^g	0.037	0.15
η @ MT ($T_{Hot} = 200-500\text{ }^{\circ}\text{C}$)	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 CO₂, 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]

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

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

973 small scale systems and the latter suitable for wearables.

974 **Conflicts of interest**

975 There are no conflicts to declare.

976 **Acknowledgements**

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