INCREASING THE EFFICIENCY OF INTERNAL COMBUSTION ENGINES: HEAT RECOVERY FROM EXHAUST GASES BY THERMOELECTRIC EFFECT[1]

MAURO FRANCESCO SGROI (*)

SUNTO. – Le crescenti preoccupazioni relative al riscaldamento globale hanno indotto una pressione legislativa sulle industrie automobilistiche per individuare soluzioni alternative e più efficienti, tese a diminuire la combustione interna nei motori. In Europa la attuale regolamentazione per i veicoli per trasporto passeggeri limita la emissione di CO_2 a un valore medio di 130 gr/km, fissando per il 2021 un obiettivo di 95 gr/km. Le industrie produttrici di automobili dovranno pagare pesanti sanzioni per la registrazione di vetture che eccedessero i limiti di CO_2 (95 Eu per ogni grammo a partire dal 2019). Le regole relative alla emissione di inquinanti (CO_2, NO_x, idrocarburi incombusti, particolati) diventano via via più stringenti e richiedono complessi e costosi sistemi di abbattimento per rispettare i limiti imposti. Da altra parte le vetture elettriche ad emissione nulla, basate su batterie, non sono ancora sufficientemente mature per sostituire i motori a combustione interna per l'uso extra-urbano, in quanto non in grado di garantire i lunghi percorsi richiesti dagli utenti. Le automobili ad idrogeno possono ottenere le stesse prestazioni delle auto tradizionali ma la penetrazione nel mercato è resa difficile dagli alti costi. Pertanto, benché caratterizzati da bassa efficienza energetica i motori a combustione interna rimarranno, almeno a medio termine, la tecnologia di riferimento per l'industria automobilistica ma le restrizioni imposte richiederanno la ibridizzazione con sistemi elettrici. La architettura ibrida permetterà di circolare in modalità elettrica in area urbana, così limitando l'inquinamento locale e incrementando la efficienza mediante ricupero della energia nel corso delle fasi di frenamento. Una analisi del bilancio energetico dei motori a combustione interna convenzionali indica che circa il 70% della energia chimica nel combustibile è convertita in energia di trasporto mentre il resto è dissipata per il 30% come calore nei gas di scarico e il 40% nel circuito di raffreddamento. In tal modo

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(*) Group Materials Labs – Engine Emission After-treatment. Centro Ricerche FIAT, Orbassano (TO), Italia. E-mail: mauro.sgroi@crf.it

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una grande quantità di energia termica è a disposizione nella automobile e il suo recupero potrebbe significativamente aumentare la efficienza del sistema. Sistemi ibridi faciliterebbero tale obiettivo poiché l'energia elettrica può essere immagazzinata in batterie. I generatori termoelettrici (TEG) offrono la possibilità di convertire direttamente la energia termica in elettricità con ridotta complessità e potenzialmente a bassi costi. Anche se le giunzioni a semiconduttore oggi disponibili sono caratterizzate da bassa efficienza e temperature di lavoro limitate, applicando i TEG ai motori a combustione interna permetterebbe il ricupero di circa 1 kW di potenza elettrica in una automobile di media dimensione, con la riduzione di CO_2 emessa di circa 10gr/km.

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ABSTRACT. – The concern related to global warming is generating a legislative pressure on reducing CO_2 emissions that is forcing automotive industry to find alternative and more efficient solutions to internal combustion engines. In Europe, the current regulation for passenger vehicles limits the CO_2 emissions calculated as fleet average to 130 g/km and fix a target value of 95 g/km to be achieved by 2021. Car manufacturers will have to pay heavy penalties for each registered vehicle exceeding the CO_2 limits (€95 per exceeding gram by 2019). Concurrently, the regulations on toxic emissions (CO, NO_x, unburned hydrocarbons, particulate matter) is also becoming more and more stringent and requires complex and costly abatement systems to respect the strict limitations imposed on NO_x and particulate matter emissions. On the other hand, zero emission electric vehicles, based on batteries, are still not mature enough for a replacement of the internal combustion engine in extra-urban applications, since they are not able to guarantee the driving range required by customers. Hydrogen fuelled vehicles, could meet the same performance of conventional cars, but the cost of materials used in the fuel cell stack is preventing the penetration into the market. Therefore, even though characterized by low energy efficiency, the internal combustion engine will remain, in the short-medium term, the reference technology for the transport industry but the environmental regulations will impose its hybridization with electric systems. Hybrid architectures allow circulating in electric mode in urban areas, limiting the local pollution, and increase the efficiency of the car through energy recovery during breaking phases. An energetic analysis of conventional internal combustion engine reveals that about 70% percent of the chemical energy stored in the fuel is converted in to mechanical energy for traction: the remaining part is dissipated as heat in the exhaust gases (30%) and in the cooling circuit (40%). So a great amount of thermal energy (tens of kW) is available on a car and its effective recovery can dramatically increase the efficiency of the system. Hybrid systems facilitate this task, since the produced electric energy can be stored in the battery pack. Thermoelectric generators (TEGs) offer the possibility to directly convert thermal energy into electricity with a reduced complexity and potential low cost. Even though available semiconducting junctions are characterized by low efficiency and limited operating temperatures, coupling a TEG to the internal combustion engine would allow recovering about 1 kW of electric power on a medium size car, with a reduction of CO_2 emissions of about 10 g/km.

GENERAL OVERVIEW

The concentration of CO_2 in the atmosphere is constantly growing from the beginning of the industrial era (see *Fig. 1*). The reduction of CO_2 emissions is mandatory for reducing the global warming and the related climatic changes.

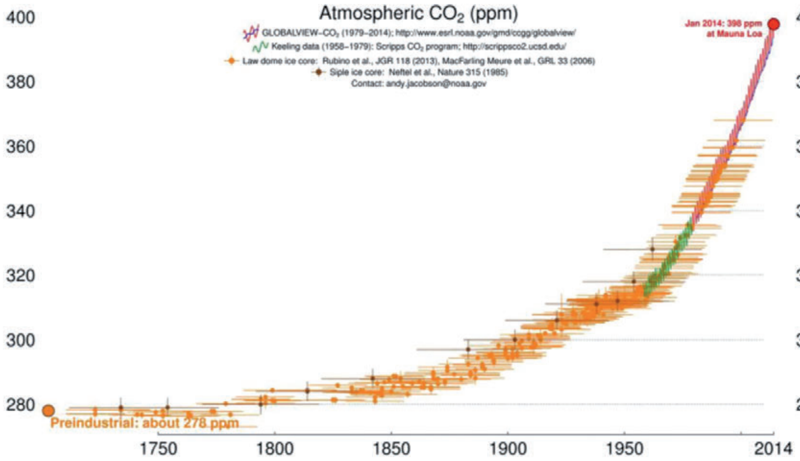
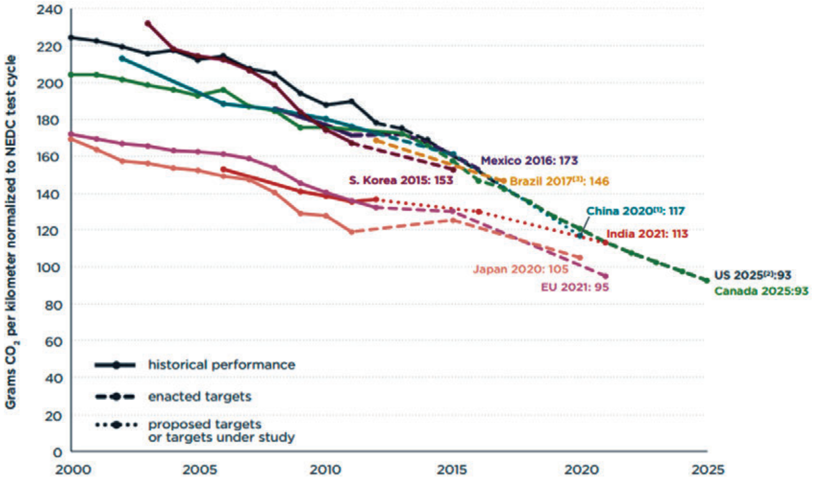


Fig. 1. Concentration of atmospheric CO_2 since the beginning of industrial era. Source: National Oceanic and Atmospheric Administration (US-NOAA).

The concern related to global warming is generating a legislative pressure on reducing CO_2 emissions that is forcing automotive industry to find alternative and more efficient solutions to internal combustion engines. In Europe, the current regulation for passenger vehicles limits the CO_2 emissions calculated as fleet average to 130 g/km and fix a target value of 95 g/km to be achieved by 2021. Car manufacturers will have to pay heavy penalties for each registered vehicle exceeding the CO_2 limits (€95 per exceeding gram by 2019). An outlook of current worldwide trends in limiting CO_2 emissions is reported in *Fig. 2*.

Concurrently, the regulations on toxic emissions (CO, NO_x, unburned hydrocarbons, particulate matter) is also becoming more and more stringent and requires complex and costly abatement systems to respect the strict limitations imposed on NO_x and particulate matter emissions. An example is the selective catalytic reduction (SCR) technology, based on the catalytic reduction of nitrogen oxides through injection of urea solutions in the exhaust gas stream. This solution, even if allowing reducing noxious emissions, greatly increases the complexity and cost of diesel vehicles.



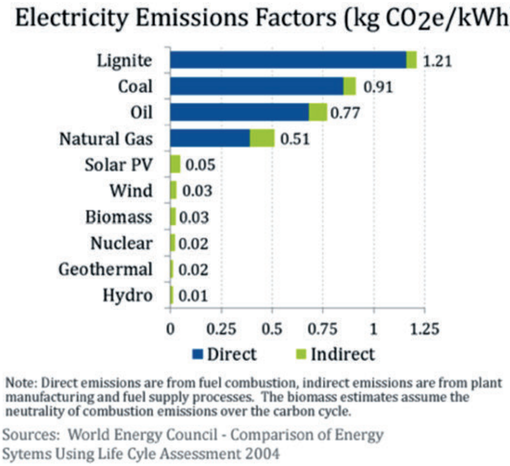
[1] China's target reflects gasoline vehicles only. The target may be higher after new energy vehicles are considered.
[2] US standards GHG standards set by EPA, which is slightly different from fuel economy stadards due to low-GWP refrigerant credits.
[3] Gasoline in Brazil contains 22% of ethanol (E22), all data in the chart have been converted to gasoline (E00) equivalent
[4] Supporting data can be found at: http://www.theicct.org/info-tools/global-passenger-vehicle-standards

Fig. 2. Trends in worldwide regulations limiting the carbon dioxide emissions from passenger vehicles.

Hydrogen fuelled vehicles, could meet the same performance of conventional cars, but the cost of materials used in the fuel cell stack is preventing the penetration into the market.

On the other hand, zero emission electric vehicles, based on batteries, are still not mature enough for a replacement of the internal combustion engine in extra-urban applications, since they are not able to guarantee the driving range required by customers. Moreover, the carbon footprint of electric vehicles strongly depends on how the electric energy is produced: the electricity emission factor ($kgCO_2/kWh$) can be higher than 1 for thermoelectric plants working with coal and lower than 0.01 for hydroelectric generation (see *Fig. 3*). For this reason, the introduction of electric vehicles in countries like China and India can worsen the global warming.

Therefore, even though characterized by low energy efficiency, the internal combustion engine will remain, in the short-medium term, the reference technology for the transport industry but the environmental regulations will impose its hybridization with electric systems. Hybrid architectures allow circulating in electric mode in urban areas, limiting the local pollution, and increase the efficiency of the car through energy recovery during breaking phases.


Electricity Emissions Factors (kg CO2e/kWh)

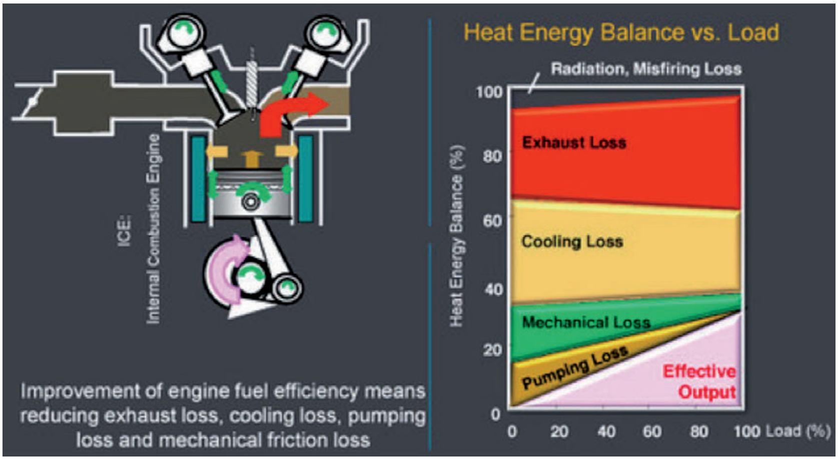
Note: Direct emissions are from fuel combustion, indirect emissions are from plant manufacturing and fuel supply processes. The biomass estimates assume the neutrality of combustion emissions over the carbon cycle.

Sources: World Energy Council - Comparison of Energy Sytems Using Life Cyle Assessment 2004

Fig. 3. Electricity emission factors of different energy generation technologies.

An energetic analysis of conventional internal combustion engine reveals that about 30% percent of the chemical energy stored in the fuel is converted in to mechanical energy for traction: the remaining part is dissipated as heat in the exhaust gases (30%) and in the cooling circuit (40%). See *Fig. 4*. So a great amount of thermal energy (tens of kW) is available on a car and its effective recovery can dramatically increase the efficiency of the system. Moreover the temperature of exhaust gases is higher than 500°C and this gives the possibility to scavenge energy efficiently using thermodynamic cycles. Hybrid vehicle architectures facilitate this task, since the recovered electric energy can be stored in the battery pack.

Thermoelectric generators (TEGs) based on the Seebeck's effect, offer the possibility to directly convert thermal energy into electricity with a reduced complexity and potential low cost. Even though available semiconducting junctions are characterized by low efficiency and limited operating temperatures, coupling a TEG to the internal combustion engine could allow recovering about 1 kW of electric power on a medium size car, with a reduction of CO_2 emissions of about 10 g/km.



Improvement of engine fuel efficiency means reducing exhaust loss, cooling loss, pumping loss and mechanical friction loss

Fig. 4. Energetic analysis of internal combustion engine.

The requirements of the automotive application are very demanding and can be summarized as follows:

- Low cost
- Limited space to install added equipment
- Resistance to shocks and vibrations
- Environment temperature range: –40°C to 50°C
- Thermal shocks: during start-up exhaust gases temperature increases from 20 to more than 500°C in less than 2 minutes
- Thermal cycling–More than 1500 cycles per year for at least 10 years
- Minimum design life 10 years or 150000 Km
- Exposure to a wide variety of fluids (water, coolant, exhaust gases, oil, etc.) either internally or externally.

SEEBECK EFFECT AND THERMOELECTRIC GENERATORS

In 1823 Seebeck found that a circuit made from two dissimilar metals, with junctions at different temperatures deflects a compass needle. The temperature difference produces an electric potential which can drive an electric current in a closed circuit. See *Fig. 5*.

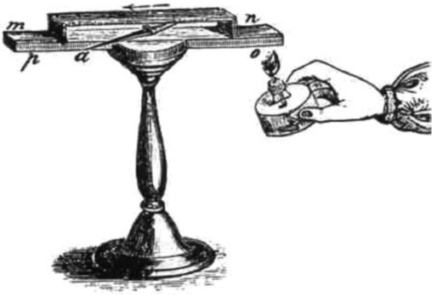


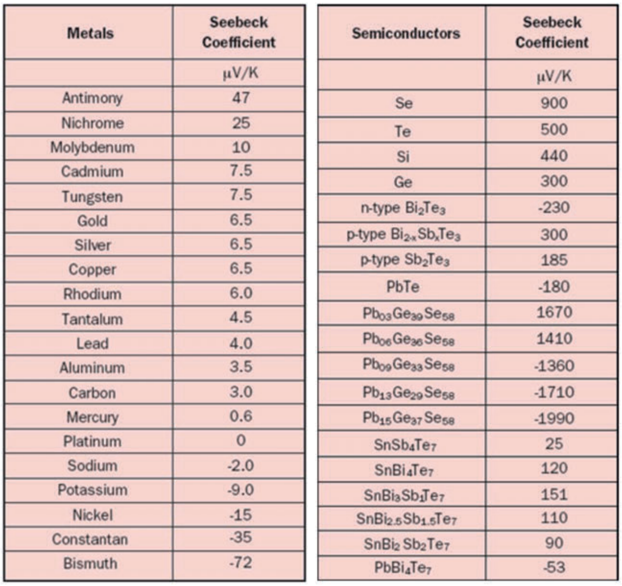
Fig. 5. Historical drawing showing the Seebeck's effect.

The ratio between the produced electric potential and the difference between cold and hot sides of the metallic junction is said Seebeck's coefficient α:

$$V=\alpha(T_h-T_c)$$

The Seebeck's coefficient of different metals and semiconductors is reported in *Tab. 1*.

Table 1. Seebeck coefficients of different materials.
Left: metals and alloys compared to Pt. Right: Semiconductors.
Source: http://www.electronics-cooling.com/2006/11/the-seebeck-coefficient



Metals	Seebeck Coefficient
	μV/K
Antimony	47
Nichrome	25
Molybdenum	10
Cadmium	7.5
Tungsten	7.5
Gold	6.5
Silver	6.5
Copper	6.5
Rhodium	6.0
Tantalum	4.5
Lead	4.0
Aluminum	3.5
Carbon	3.0
Mercury	0.6
Platinum	0
Sodium	-2.0
Potassium	-9.0
Nickel	-15
Constantan	-35
Bismuth	-72

Semiconductors	Seebeck Coefficient
	μV/K
Se	900
Te	500
Si	440
Ge	300
n-type Bi_2Te_3	-230
p-type $Bi_{2-x}Sb_xTe_3$	300
p-type Sb_2Te_3	185
PbTe	-180
$Pb_{03}Ge_{39}Se_{58}$	1670
$Pb_{06}Ge_{36}Se_{58}$	1410
$Pb_{09}Ge_{33}Se_{58}$	-1360
$Pb_{13}Ge_{29}Se_{58}$	-1710
$Pb_{15}Ge_{37}Se_{58}$	-1990
$SnSb_4Te_7$	25
$SnBi_4Te_7$	120
$SnBi_3Sb_1Te_7$	151
$SnBi_{2.5}Sb_{1.5}Te_7$	110
$SnBi_2Sb_2Te_7$	90
$PbBi_4Te_7$	-53

Semiconducting materials have better Seebeck's coefficients than metals and modern thermoelectric modules are made of n- and p-type semiconductors connected electrically in series and thermally in parallel. With thermoelectric modules it is possible to realize a thermoelectric generator implementing a **thermodynamic cycle** converting heat directly into electric energy with **no moving parts**. As for all thermodynamic cycles, the maximum theoretical efficiency is limited by **Carnot's efficiency**. Thermoelectric generators are very simple, durable and reliable but suffer from high cost of materials and low efficiency (typically below 5%). A thermoelectric generator can be coupled with a heat exchanger collecting energy from exhaust gases coming from internal combustion engines. The cycle works between the temperature of exhaust gases and the ambient temperature (see *Fig. 6*).

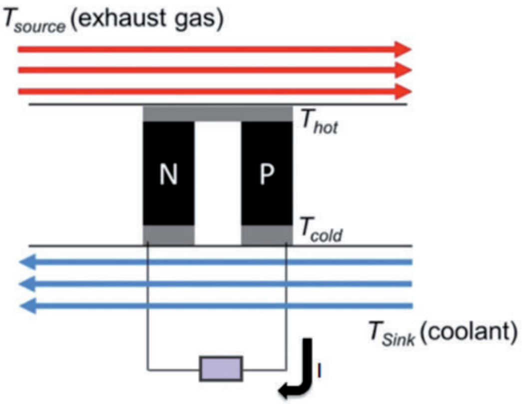


Fig. 6. Principle of electric generation with thermoelectric modules.

The efficiency η_{TEmax} of a thermoelectric generator made of n- and p-type semiconducting materials is given by the formula[2]:

$$\eta_{TEmax} = \frac{W_{elec}}{Q_H} = \frac{\Delta T}{T_H} \cdot \frac{\sqrt{1+Z\bar{T}}-1}{\sqrt{1+Z\bar{T}}+\frac{T_C}{T_H}} \quad \text{with}$$

$$Z = \frac{(\alpha_p - \alpha_n)^2}{\left((\lambda_p.\rho_p)^{1/2} + (\lambda_n.\rho_n)^{1/2}\right)^2} \qquad \mathrm{T} = (T_H - T_C)/2 \qquad \Delta T = T_H - T_C$$

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[2] Min G. In: Rowe DM, editor. Thermoelectrics Handbook Macro to Nano. CRC Press; 2006.

Where:

- W_{elec} electric energy produced
- Q_h thermal energy entering the hot face
- T_H (T_C) temperature of the hot (cold) side of the TE modules
- **ZT** is the **dimensionless figure of merit** of the TE materials. It ranges usually between 0.5 and 1.5.
- ρ_p and ρ_n electrical resistivities
- λ_p and λ_n thermal conductivities
- α_p and α_n Seebeck coefficients

Fig. 7 reports the efficiency of the thermoelectric generator versus the difference T_H-T_C for various values of ZT.

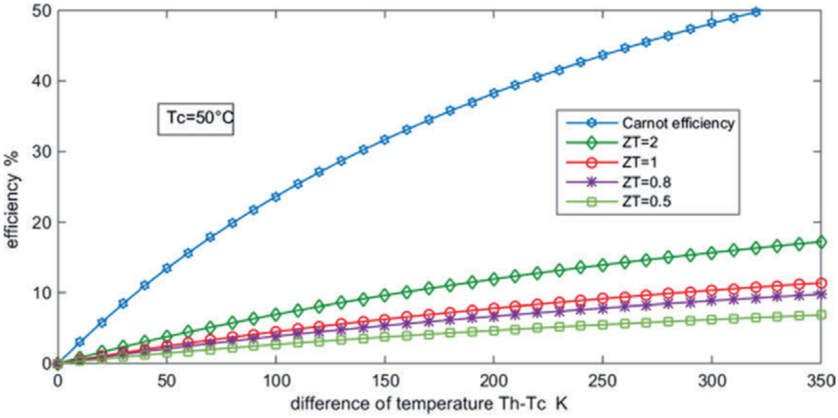

Fig. 7. Efficiency of thermoelectric generators with different ZT versus *$\Delta T=T_H$-T_C. Thermal sink at temperature T_C=50°C.*
Source: Thermoelectric generators: A review of applications, Daniel Champier, Energy Conversion and Management 140 (2017), pp. 167-181.

It is evident that to increase the efficiency of the system, materials able to work at high temperature and characterized by high values of ZT are required. On the other hand Nature seems to prevent increasing the value of ZT above values of 1.5-2. In fact the total thermal conductivity of a material is given by the electronic and phononic contributions:

$$\lambda_{tot} = \lambda_{ph} + \lambda_{el}$$

But the Wiedeman-Franz law states that the ratio of the electronic contribution of the thermal conductivity (λ_{el}) to the electrical conductivity (σ) of a metal is proportional to the temperature (T)[3]:

$$\lambda_{el}=L\sigma T$$

where L is the Lorentz number. So increasing the electronic conductivity of the material (which means to decrease its resistivity) implies necessarily to increase also the thermal conductivity. This implies to have a counterbalancing of effects in the formula for ZT. Thus the only way to enhance ZT is to minimize the lattice thermal conductivity by increasing the phonon scattering. Current approaches to do this are based on the introduction of heavy atoms in the crystal lattice or on the nanostructuring of the material to increase phonon scattering. *Fig. 8* reports typical values of ZT for the most studied semiconducting materials.

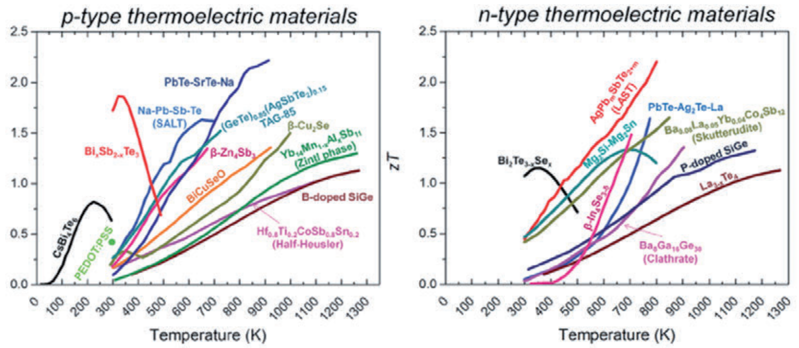

Fig. 8. ZT values of p-type and n-type semiconducting materials versus *temperature.*
Source: "Skutterudites as thermoelectric materials: revisited", M. Rull-Bravo, A. Moure, J.F. Fernández and M. Martín-González, RSC Advances, 52, 2015, DOI:10.1039/C5RA03942H.

Automotive exhaust heat recovery from exhaust engine gases requires **high operating temperature, low cost** and the use of **non-toxic** and **available raw materials.** For these reasons the most promising materials are Si-Ge and Mg_2Si alloys.

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[3] Jones, William; March, Norman H. (1985). Theoretical Solid State Physics. Courier Dover Publications. ISBN 0-486-65016-2.

Several automotive OEMs are currently working on thermoelectric heat recovery. *Fig. 9* shows some prototypes developed by different automotive companies.

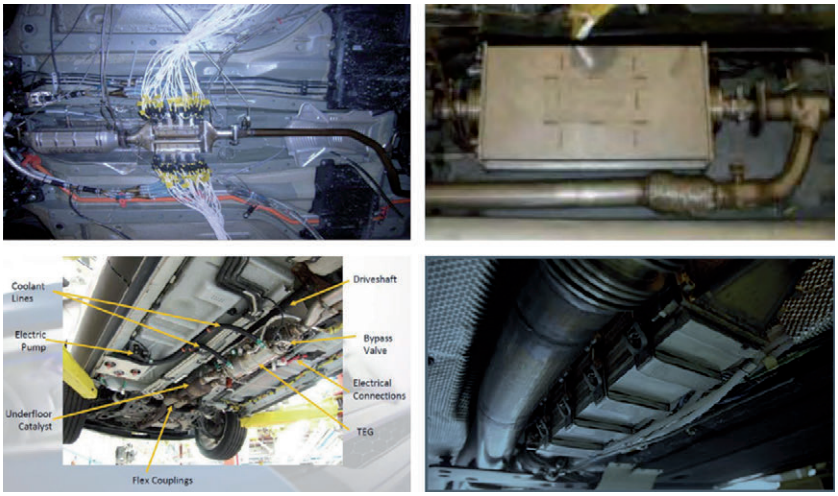

Fig. 9. Examples of automotive TEGs.
Top right: Honda. Top left: GM. Bottom right: Ford. Bottom left: BMW.

Centro Ricerche FIAT was involved in the HEATRECAR European project ("Reduced energy consumption by massive thermoelectric waste heat recovery in light-duty trucks") aiming at using thermoelectric cells for converting the waste heat in the exhaust line of internal combustion engines into electric power for reducing fuel consumption and emission of pollutants. Four different thermoelectric material classes suitable for low temperature (Bi_2Te_3) and high temperature (PbTe, TAGS-85, skutterudites) were synthesized and characterized by the project consortium. Bi_2Te_3 based modules were selected for building the final TEG prototype. The TEG was able to deliver 500W at the design point, with inlet gas at 450°C and a mass flow rate of 90 g/s and was installed on a IVECO Daily with a diesel engine (see *Fig. 10*). On the NEDC homologation cycle the thermoelectric system dropped the fuel consumption by about 2.2% (6.7 g CO_2/ km reduction) with a peak thermoelectric electric power of 150 W. On the more demanding WLTP Cycle the system reduced the fuel consumption by about 3.9% (9.6 g CO_2/km reduction) with a maximum thermoelectric electric power of 200 W. As a matter in highway conditions the TEG power is sufficient to provide the on-board electric needs, completely replacing the alternator.

Fig. 10. Left HEATRECAR prototype TEG. Right Iveco Daily integrating the TEG.

CONCLUSIONS

Thermoelectric energy recovery in automotive applications is extremely promising for reducing the carbon footprint of vehicles and many OEMs are developing original solutions. On the other hand commercial thermoelectric modules have ZT lower than 1.5 and operating temperature limited to 300°C, allowing reaching a maximum conversion efficiency of 5%. With these performances a 4% reduction of CO_2 emissions of internal combustion engine vehicles is already possible. Moreover TEG generators can be effectively integrated in hybrid vehicles since the produced electric power can be used to recharge the battery pack.

Despite these considerations, the high cost of materials and the limited operating temperature and efficiency are still preventing the large scale application of TE technology in automotive field. For this reason further research on materials is required to develop affordable and high performing solutions compliant with the strict requirements of industry.