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

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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 l’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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una grande quantità di energia termica è a disposizione nella automobile e il suo ricupero 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 CO₂ emessa di circa 10 gr/km.

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ABSTRACT. – The concern related to global warming is generating a legislative pressure on reducing CO₂ 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 CO₂ 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 CO₂ limits (€ 95 per exceeding gram by 2019). Concurrently, the regulations on toxic emissions (CO, NOₓ, 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 NOₓ 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 CO₂ emissions of about 10 g/km.
GENERAL OVERVIEW

The concentration of $\text{CO}_2$ in the atmosphere is constantly growing from the beginning of the industrial era (see Fig. 1). The reduction of $\text{CO}_2$ 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).](image)

The concern related to global warming is generating a legislative pressure on reducing $\text{CO}_2$ 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 $\text{CO}_2$ 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 $\text{CO}_2$ limits (€95 per exceeding gram by 2019). An outlook of current worldwide trends in limiting $\text{CO}_2$ emissions is reported in Fig. 2.

Concurrently, the regulations on toxic emissions ($\text{CO}$, $\text{NO}_x$, 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 $\text{NO}_x$ 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.

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 (kgCO₂/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.

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.

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: $-40^\circ$C to $50^\circ$C
- Thermal shocks: during start-up exhaust gases temperature increases from 20 to more than 500$^\circ$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.
The ratio between the produced electric potential and the difference between cold and hot sides of the metallic junction is said Seebeck’s coefficient $\alpha$:

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

The Seebeck’s coefficient of different metals and semiconductors is reported in Table 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*
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).

![Principle of electric generation with thermoelectric modules.](image)

The efficiency $\eta_{\text{TE}_{\text{max}}}$ of a thermoelectric generator made of n- and p-type semiconducting materials is given by the formula:\(^2\)

$$\eta_{\text{TE}_{\text{max}}} = \frac{W_{\text{elec}}}{Q_H} = \frac{\Delta T}{T_H} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_C}{T_H}}$$

with

$$Z = \frac{(\alpha_p - \alpha_n)^2}{((i_p \rho_p)^{1/2} + (i_n \rho_n)^{1/2})^2}$$

$$T = (T_H - T_C)/2 \quad \Delta T = T_H - T_C$$

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Where:
- \( W_{\text{elec}} \) 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.
- \( \rho_p \) and \( \rho_n \) electrical resistivities
- \( \lambda_p \) and \( \lambda_n \) thermal conductivities
- \( \alpha_p \) and \( \alpha_n \) 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](image.png)

**Fig. 7. Efficiency of thermoelectric generators with different \( ZT \) versus \( \Delta T = T_H - T_C \).**

Thermal sink at temperature \( T_C = 50^\circ \text{C} \).


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:

\[
\lambda_{\text{tot}} = \lambda_{\text{ph}} + \lambda_{\text{el}}
\]

But the Wiedeman-Franz law states that the ratio of the electronic
contribution of the thermal conductivity ($\lambda_{el}$) to the electrical conductivity ($\sigma$) of a metal is proportional to the temperature ($T$):

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

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 nano-structuring 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$_2$Si alloys.

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

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$_2$Te$_3$) and high temperature (PbTe, TAGS-85, skutterudites) were synthesized and characterized by the project consortium. Bi$_2$Te$_3$ 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 maxi-
mum 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.](image)

**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 CO₂ 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.