STUDY OF A THERMOELECTRIC GENERATOR BASED ON A CATALYTIC PREMIXED MESO-SCALE COMBUSTOR

L. Merotto¹ , C. Fanciulli² , R. Dondè¹ , and S. De Iuliis¹ ¹ CNR – IENI (Istituto per l'Energetica e le Interfasi), via Cozzi 53, 20125 Milano, Italy ² CNR-IENI Corso Promessi Sposi 29, 23900, Lecco, Italy *merotto@ieni.cnr.it

Abstract

 The recent advances in miniaturized mechanical devices open exciting new opportunities for combustion, especially in the field of micro power generation, allowing the development of power-13 supply devices with high specific energy. The development of a device based on a catalytic combustor
14 coupled with thermoelectric modules is particularly appealing for combustion stability and safety. coupled with thermoelectric modules is particularly appealing for combustion stability and safety. Furthermore, when implemented in micro/meso scale devices, catalytic combustion allows full utilization of hydrocarbon fuel's high energy densities, but at notably lower operating temperatures than those typical of traditional combustion. These conditions are more suitable for coupling with conventional thermoelectric modules since they prevent the modules' degradation.

 In this work a novel catalytic meso-scale combustor fueled with propane/air mixture has been coupled with two conventional thermoelectric modules. The wafer-like combustor is filled with commercially 21 available catalytic pellets of alumina with Platinum (1% weight). Temperature measurements, in terms
22 of point values and 2D distribution across the combustor surfaces, were carried out in different operating of point values and 2D distribution across the combustor surfaces, were carried out in different operating conditions. Exhaust gases concentration measurements and pellet aging investigation were performed to determine the combustor efficiency and stability. Starting from these results the combustor has been coupled to bismuth telluride-based thermoelectric modules using a water cooled heat exchanger at the 26 cold side. The system obtained produces 9.86 W of electrical power reaching an overall efficiency up to 2.85%: these results represent an improvement in portable-scale electrical power production from hydrocarbon fuels state-of-art. Moreover, the voltage and current characteristics allow using such generator for small portable devices power supplying.

Keywords

 Thermo-electric generator, portable energy production, meso-scale catalytic combustor, propane catalytic combustion

Introduction

 During the last few years, the miniaturization of mechanical and electromechanical engineering devices has received growing attention thanks to the increasing interest in the areas of microelectronics, 38 biomechanics, molecular biology, as well as thanks to the progress made in microfabrication techniques
39 [1]. The advances in miniaturized mechanical devices open exciting new opportunities for combustion, [1]. The advances in miniaturized mechanical devices open exciting new opportunities for combustion, especially in the field of micro power generation [2,3], allowing the development of power-supply devices with high specific energy (small size, low weight, long duration) [4,5]. Due to the small scale, effects of flame-wall interaction and molecular diffusion become more significant in micro and meso- scale combustion [2,4] when compared to traditional combustion systems. These effects are still not completely understood and require further investigation.

 Even at 10% energy conversion efficiency, hydrocarbon fuels can provide 10 times the energy density of the most advanced batteries [6-8]. Therefore, hydrocarbon-based devices as portable power sources [7-9] can be considered as a suitable alternative to common batteries. In this context, both homogeneous combustion [10-16] and catalytic reactors [17-22] are of major interest. These systems are used either for hydrogen generation for fuel cells [23-27] or for direct conversion of thermal energy released via combustion to electrical energy using thermoelectric or thermo-photovoltaic devices [28-

30].

 The major drawback of conventional homogeneous (gas-phase) combustion systems lies in the very high (>1500ºC) operating temperatures. These high temperatures greatly limit material selection and require extensive combustor insulation. Further strong limitations of these devices are strictly related to their dimensions. As the size decreases, the surface area-to-volume ratio of the combustor increases with a subsequent increase of the heat-loss to heat-generation ratio. These strong losses in the small dimension induce flame quenching [1-3], and are also responsible for an increase in pollutants emission such as CO and unburned hydrocarbons. In addition, the smaller the volume, the shorter the flow residence time. To overcome such limitations, catalytic combustion seems to be the most suitable solution [31,32]. When implemented in micro/meso scale devices, catalytic combustion allows full utilization of the high energy densities of hydrocarbon fuels, but at notably lower operating temperatures than those typical of traditional combustion. Additionally, catalytic systems are generally easier to start, more robust to heat losses, and self-sustained at leaner fuel/air ratios [33-36].

 When characterizing a catalytic combustor, catalyst degradation needs to be addressed [37]. The main mechanisms for platinum catalyst degradation include particle agglomeration, platinum loss and redistribution, and poisonous effects due to contaminants [38]. The catalyst degradation can be affected by the operating conditions, including temperature, humidity, and sources of contamination of catalyst active sites. Some studies concerning platinum aging show that no great effect on Pt catalyst is detected 69 at automotive normal operating temperature $(500^{\circ}C)$, with consequently no substantial change in overall system performance [39]. Despite the huge amount of literature on catalyst degradation, no results for tests performed in conditions similar to those addressed in this work are available in literature. Therefore, in the present work, degradation tests were carried out on catalytic pellets.

 In order to investigate the overall performance of a catalytic meso-scale combustor, the analysis of exhaust gases is required to derive chemical efficiency. Fourier transform infrared spectroscopy (FT- IR) has been widely applied for quantitative measurement of gas species concentrations of vehicles's exhaust [40,41]. Nevertheless, only a few works, such as [30], are reported in literature regarding the application of the FT-IR technique to measure gases concentration at the exhaust of a meso-scale combustor.

 Compared to fuel cells or other combustion-based systems, thermoelectric (TE) power generators are attractive for portable systems due to their compactness, their reliability, their low energy consumption, and their high power densities. Considering commercial bismuth telluride-based TE 82 modules, the operating temperature range is limited to 250°C, which is incompatible with the temperatures of a standard combustor. So, catalytic combustion is particularly well suited for TE power generation because of this relatively low temperature ceiling.

 There are many examples of micro- and mesoscale thermoelectric power generators powered by catalytic combustion in available literature [42-46]. A TE generator fabricated from silicon bonded to glass developed by Yoshida et al. [46] was able to produce 184 mW of electrical power with an efficiency of 2.8% from the catalytic combustion of hydrogen. Norton and co-workers [5] reported for their integrated combustor-TE generator the production of 1W maximum power and a thermal-to- electrical conversion efficiency of 1.08% with hydrogen as the fuel. The group has also reported the generation of 0.45 W electrical power with propane as the fuel at 0.42% conversion efficiency, using propane lower heating value LHV [27]. In recent years, Marton and co-workers [47] developed a butane- fueled thermoelectric generator (TEG) delivering 5.82 W maximum power with 2.53% conversion efficiency. Several efforts have been made by different authors to investigate the hot gases recirculation in order to reduce heat losses and thus increase the efficiency of this kind of systems [48-50]. Nevertheless, the demonstration of a fuel-based TEG suitable for portable power with energy density comparable to that of a battery remains an open challenge.

 In this work, a new premixed catalytic combustor has been developed and characterized. The device has been designed for coupling with thermoelectric modules for portable electrical power production. The combustor is used as heat source in a sandwich between two TE modules, in order to achieve a larger electrical power output, with I-V characteristics suitable for supplying small electrical devices. Since the voltages obtained with small thermoelectric devices are usually too low for direct utilization, this feature is one of the most important advantages offered by the TEG presented in this work.

 The meso-combustor developed in this work has notable advantages when compared to similar solutions presented in the literature [5-7]. The first advantage is the use of a low-cost, commercially available catalyst, with no need for *ad hoc* manufacturing. The second important advantage is that the

use of such a catalyst allows obtaining the desired wall temperatures for thermoelectric device coupling

with no need for wall insulation from higher temperatures, thus resulting in smaller fuel consumption

and a more compact design. The commercial TE modules chosen are not specifically designed for power

 applications, but the refined thermal control of the combustor allows producing up to 9.86 W of electrical power with a thermal to electrical conversion efficiency of 2.85%, resulting in an improvement in

portable-scale electrical power converters based on thermoelectric technology and hydrocarbon fuels.

Materials and Methods

 A thermoelectric generator was designed coupling a catalytic premixed meso-scale combustor and thermoelectric commercial modules. The sketch of the TEG developed is reported in Figure 1. Two TE modules are placed in a thermal chain consisting of the catalytic combustor surfaces (hot side) and two water-cooled heat sinks (cold side). In order to provide the most efficient contact at the interfaces 118 between the TE modules with the combustor surface and the heat sink, graphite sheets (100 µm thick) are used. Graphite was chosen for its capability for compensating the effects of surface roughness and was preferred to thermal pastes for its high reproducibility and stability. The heat sinks are aluminum 121 bulks homogeneously cooled by a 13 \degree C water flowing in the circuit at 6 l/min volume rate. The cooling system is arranged in order to provide similar thermal conditions at both TEG sides. To ensure the thermal chain, the system is held together by two metal springs and four bolds and nuts. The compressive system allows obtaining a homogeneous pressure on the surfaces, minimizing thermal losses, compensating the increase of pressure on the TE modules due to the thermal expansion, and preserving 126 the thermal chain components' correct alignment. In this work, $40 \times 40 \text{ mm}^2$ Ferrotec commercial modules based on chalcogenides are used. These modules are designed for cooling applications, so no 128 data specific for power generation are available. The operative limits below 260 \degree C considered in this work are derived considering the technologies used for thermoelectric elements soldering inside the device. Moreover, each module has been tested in order to define the conversion capability of the device, obtaining a response in terms of Seebeck effect of 30 mV/K and an internal resistance, useful for 132 maximum power at the matching load calculation, of 3.94Ω . The power output is a function both of the 133 load and of the ΔT applied to the module: using a $\Delta T = 150$ °C, the maximum power produced by a single module is in the order of 3.8 W corresponding to a V-I couple of 3.5V and 1.1A, respectively.

Figure 1. Sketch of the thermoelectrical generator obtained by coupling the combustor with two commercial thermoelectic modules.

 The catalytic premixed meso-scale combustor was designed and characterized to be coupled to the TE modules [51]. The investigation was performed in order to assess the feasibility of the meso-scale combustor for the limits imposed by the modules used. Devices similar to the one presented in this work were proposed in [5], where the combustion channel is less than 1 mm high and the temperature at the combustor walls is too high for a direct coupling with thermoelectrics, thus requiring an intermediate cooling step. In the present work, the experimental conditions (e.g. combustion channel size, fuel/air

 mass flow rates, etc) were chosen in order to reach the desired temperature without any cooling system at the interface between combustor and TE modules.

 In Figure 2 a sketch of the combustor is shown. The geometry used for the combustion chamber was chosen in order to match the size of the TE devices. The aluminum-made combustor has a 40 x 40 146 x 4 mm³ chamber filled with 155 commercial alumina cylindrical pellets (r = 1.6 mm, h = 3.2 mm) covered with a thin catalytic film (platinum 1 % weight). The pellets are placed in ordered lines so that the height of the channel for gas flowing is 0.8 mm. Propane and air are used as fuel and oxidizer, and the related mass flow rates are measured and controlled by using thermal mass flow meters (Bronkhorst 150 El-Flow F-201CV). As C_3H_8/air mixture is not self-igniting in contrast with H_2/air mixture, hydrogen assisted ignition is performed.

 The wall temperature distribution was measured with a Flir Systems Thermovision A40 thermo camera using the values from K-type thermocouples placed on the combustor surface (A, B and C positions in Fig. 2) as absolute temperature reference for calibration. The accuracy in point 155 measurements is about $0.5\% \pm 2^{\circ}\text{C}$ in the temperature range considered (from -20 $^{\circ}\text{C}$ to +350 $^{\circ}\text{C}$).

 The overall chemical efficiency was estimated by means of Fourier transform infrared spectrometry (FT-IR) analysis of the exhaust gases. The exhaust gases were sent through a cut-off particulate filter and a water trap to a Thermo Scientific Nicolet 6700 FT-IR spectrometer equipped with a variable- pathlength heated gas-cell (Gemini Mars series 6.4M, internal volume of 0.75 l) positioned inside the instrument. In order to prevent possible carbon-residuals condensation, both the transfer line and the gas-cell were maintained at 393 K. To avoid exhaust gases dilution with ambient air, the suction mass flow was set to 6 Nl/min to be lower than the outlet mass flow. The FT-IR spectra have a resolution of 163 . 0.5 cm⁻¹. The background was obtained with N_2 flow and subtracted from the spectra. Quantitative analyses of the gas concentrations were performed referring to a calibration based on mixtures of known 165 compositions. The process chemical efficiency, η_c , was calculated using the relationship:

166
$$
\eta_c = \frac{[CO_2]}{[CO_2] + [CO] + [UHC]} \qquad \text{Eq. (1)}
$$

where [UHC] is the concentration of the total unburned hydrocarbons.

Figure 2. Sketch of the meso-scale combustor used in this work: the positions of the thermocouples used to measure the combustor wall temperature are indicate with A, B, C and D.

 A peculiarity of thermoelectric technology is its long life with no need for maintenance. In order to consider the catalytic combustor a suitable heat source for the TEG, it was necessary to study the combustor components aging effects under operative conditions. In particular, attention was focused on the pellets used. An investigation of combustion processes effects on the degradation of the pellets catalytic coating was performed with metallographic analyses by using a scanning electron microscope (SEM) (FEG Hitachi SU-70) equipped with EDS and STEM detector.

- The combustor was characterized at different operating conditions with the total mass flow rate 176 ranging between 1.7 x 10⁻⁵ and 2.5 x 10⁻⁵ kg/s varying the equivalence ratio, Φ , in the range 0.8-1.2 by changing both the propane and the air mass flow rate.
- The TEG performance investigation was carried out at different operating conditions of the catalytic 179 combustor with the total mass flow rate ranging between 6.3 x 10^{-5} and 14.6 x 10^{-5} kg/s, keeping Φ at 180 stoichiometric condition. Control of the final ΔT applied to the TE modules was achieved varying the inlet total mass flow rate, increasing in this way the hot side temperature. The cold side temperature remained constant during the characterization process, due to the power removed by the water cooled circuit, proving that the good thermal coupling of the TEG's different elements allowed obtaining a good control of the stability at the cold side of the system. The TEG electrical output was studied in 185 terms of voltage and power produced for each ΔT applied. The I-V and I-W characteristics were measured at thermally steady conditions by connecting the TEG output to external loads having increasing values from short-circuit up to open-circuit.
- The data obtained from combustor and TEG characterization allowed calculating the electrical conversion efficiency for each module and for the overall device.

Results and Discussion

 The first step of the combustor characterization was assessing the total mass flow rate in order to verify the temperature on the external walls at different conditions. Preliminary tests showed that the 193 lower combustion stability limit is at $\Phi = 0.8$, for 2.5 x 10⁻⁵ kg/s mass flow rate.

 In Figure 3, the temperature values measured in the four positions versus Φ for three different total 195 mass flow rates $(1.7 \times 10^{-5} \text{ kg/s}, 2.1 \times 10^{-5} \text{ kg/s}$ and $2.5 \times 10^{-5} \text{ kg/s}$) are shown. The uncertainty in the 196 measured temperatures is approximately 6.67% in the worst case. Using 50.35 x 10⁶ J/kg for the propane calorific value, thermal power values between 62 and 95 W were obtained for total mass flow rates 198 ranging from 1.7 x 10^{-5} kg/s to 2.5 x 10^{-5} kg/s, respectively.

Figure 3. Temperature vs equivalence ratio at four different locations on the combustor wall and at three different mass flow rates.

201 As it can be noted, wall temperature increases with Φ up to $\Phi = 1$, then remains approximately constant for higher values. The behavior is similar for the three flow rates investigated at all positions. The temperature slightly decreases moving downward from the inlet at fixed flow rate, and increases 204 monotonically with the flow rate. Exhaust gases temperature values are typically slightly above 300 °C, which is higher than the walls temperatures in each condition.

206 The 2D temperature mapping on the combustor external walls is reported for different flow rates in 207 Figure 4. Only the actual combustion chamber surface has been considered. The arrows refer to the Figure 4. Only the actual combustion chamber surface has been considered. The arrows refer to the 208 mixture inlet and outlet. The actual inlet in the combustor is placed horizontally (45° rotation with 209 respect to the Figure).

 The thermocamera images were calibrated using the thermocouple data previously described. Investigation performed on both combustor sides showed no significant differences. The results prove that the temperature on the external surface of the wall is satisfactorily uniform, thus confirming that the meso combustor is a suitable hot source for the TEG. It can be noticed that the obtained temperature is lower than the typical propane catalytic reaction temperature (700-800°C). This can be explained taking into account the heat dissipation occurring at the combustor surface due to the thermal exchange with ambient air. Considering the higher temperatures obtained at the combustor outlet (Figure 3), it is reasonable to assume that the internal temperature matches the catalytic reaction temperature found in literature.

219

Figure 4. Temperature distribution on the combustor chamber external walls at three different mass flow rates. Arrows show gas inlet and outlet direction. Circles highlight the average temperature obtained in each case. Temperatures are given in Celsius degrees.

220

221 The FT-IR spectra of the gases collected at the exhaust of the premixed meso-scale combustor were 222 analyzed to determine their composition. After calibration, it was possible to perform quantitative 223 analyses with an estimated accuracy below 1% for FT-IR measurements.

²²⁴

225 In Figure 5 propane concentration versus Φ is reported for the three mass flow rates investigated. 226 In all cases, propane concentration profile shows a minimum at $\Phi = 1$ as expected. For lower and higher 227 equivalence ratios, higher unburned propane was found at the combustor outlet. At $\Phi = 1$, the unburned 228 propane increases with the decrease of the mass flow rate, ranging from about 490 ppm for 2.5×10^{-5} 229 kg/s mass flow rate to 940 ppm for 1.7×10^{-5} kg/s. The measurements error is small, with the uncertainty 230 in C_3H_8 concentration being about 7.5% in the worst case.

 CO² and CO concentrations were also measured. In both cases they increase with Φ, reaching a 232 plateau above $\Phi = 1$. The same behavior was obtained changing the mass flow rate values.

 Taking into account the concentration measurements, it is possible to evaluate the chemical efficiency given by Eq. (1) where propane is the only unburned hydrocarbon detected. In Figure 6, efficiency vs. equivalence ratio is shown for all the tested flow rates. The uncertainty in the efficiency value is 0.5% in the worst case. A slight dependence on Φ was observed, showing a maximum at the stoichiometric condition where about 96% efficiency is reached. For higher and lower Φ values, efficiencies around 92-94% are obtained. Similar values of this chemical efficiency have been reported in literature [5], referring to a different combustor fueled with the same mixture at higher flow rates.

 The results reported for the catalytic combustor characterization prove that the system thermal control and homogeneity are suitable for coupling the combustor with TE modules obtaining good chemical efficiency.

 As complementary analyses to evaluate the combustor life span, tests on pellet degradation were performed. The pellets underwent 200 h operating combustion conditions, and the evolution of the active phase was verified with SEM analyses. It is reasonable to expect that the degradation takes place at 246 typical temperature values of catalytic combustion (e-g. 700-800 °C) [35]. In these conditions, coking, agglomeration and contamination effects of the catalytic pellets are likely to occur, which could affect 248 the performance of the overall system.

 SEM images (backscattered electrons) for fresh and used (200 h) pellets surfaces are shown in Figure 7. It can be noted that used pellets show white agglomerates spread over the surface which do not appear on the fresh pellets surface. EDX analyses suggest that these agglomerates consist of Platinum, while the main material is almost entirely alumina.

Figure 7. SEM backscattered micrographs of fresh (left) and 200 h aged (right) pellet base surface.

Figure 8. EDX mapping of Pt distribution on fresh (left) and 200 h aged (right) pellets surface.

 Pt distribution mapping of the pellets' surface (Figure 8) highlights that very small Pt spots are spread on the fresh pellets' surface, while the used pellets' surface shows fewer but much larger Pt 258 structures reaching a size of $2-3 \mu m^2$. Thus, the pellets morphology evolves in operating time due to the

259 combustion temperature and the catalyzer aggregates forming particles which could affect its efficiency

260 in supporting the combustion. However, after 200 h the combustor performances seemed not to be

261 affected by this evolution and the combustor maintains its characteristics.

262

263 In Figures 9 and 10, the results of the characterization of the coupled system, catalytic combustor 264 and TE modules, in terms of electrical output of the TEG are reported. The output voltage (V) and the 265 electrical power (W), respectively, are plotted as a function of the current produced for different ΔT 266 applied. The maximum power delivered by the device ranges between 5 and 10 W for ∆T values ranging 267 between 100 and 200°C. Correspondingly, the voltage drop across the load is in the range 7.5 – 10 V. 268 The values obtained are consistent with the preliminary characterization at different thermal conditions 269 performed on the commercial modules used.

 The experiments on the TEG were performed for different total (propane + air mixture) mass flow rates resulting in different ∆T between the hot and cold sides. Experimental parameters for the different tests and the results obtained are summarized in in Table 1. Each total mass flow rate condition was obtained keeping Φ constant at stoichiometric conditions and by varying the propane and air mass flow 274 rates.

- 275
-

276 **Table 1**. Maximum TE power obtained, power provided, and conversion efficiency at different 277 mass flow rate and ∆T values.

mixture mass flow rate Kg/s	ΔT $\rm ^{\circ}C$	T_{hot} $\rm ^{\circ}C$	power provided W	power obtained W	conversion efficiency $\frac{0}{0}$
6.3×10^{-5}	100	179	178.71	5.06	2.83
8.4×10^{-5}	130	207	238.29	6.78	2.85
10.3×10^{-5}	155	233	297.86	8.24	2.77
12.6×10^{-5}	190	245	357.43	9.24	2.59
14.6×10^{-5}	200	258	417.00	9.86	2.36

278

279 It can be noted that all the mass flow rate conditions used for TEG characterization are higher than 280 those previously reported for the combustor alone. This is because when the combustor is coupled with 281 the TE modules and the cooling system, the desired temperature at the combustor surface (up to 250°C) 282 at the hot side) is obtained for higher flow rates due to the increased thermal exchange. The minimum 283 mass flow rate (6.3 x 10^{-5} kg/s) corresponds to the limit under which the combustion is no longer 284 sustained, while the maximum mass flow rate (14.6 x 10⁻⁵ kg/s) is the limit over which no further ΔT 285 increase is obtained with the cooling system used.

Figure 11. Power provided to the TEG (based on LHV) and power obtained vs. mixture mass flow rate.

Figure 12. Efficiency of thermal to electric power conversion vs. mixture mass flow rate.

 The power provided to and the power delivered from the device are plotted in Figure 11 as a function of total mass flow rate. It can be noted that the obtained power curve slope tends to decrease for higher mass flow rates, indicating that the system is approaching its maximum performance at the given cooling 290 conditions. No higher mass flow rate was tested in this work because at 14.6×10^{-5} a combustor surface temperature of 255°C was reached, which is the maximum allowed for the TE modules used. The 292 uncertainty on the experimental point is ± 2 W for the power provided to the system and ± 0.8 for the power obtained.

 In order to obtain the device thermal to electrical conversion efficiency, the power provided to the system was calculated as the propane mass delivered in each testing case times its lower heating value (LHV). Figure 12 shows the thermal to electrical conversion efficiency obtained for the different mass flow rate values tested. The maximum efficiency obtained is around 2.85%. Similar values are obtained 298 for mass flow rates values up to 10.3×10^{-5} kg/s, while for higher mass flow rates the efficiency tends to decrease. This behavior can be explained considering the effect of increased mass flow rate on exhaust concentration described before: unburnt propane concentration increases with increasing mass flow rates due to the reduced residence time. This leads to a lower propane conversion efficiency which negatively affects the thermal to electrical conversion.

 A comparison with similar devices described in literature is shown in Table 2, in which the overall power produced and the thermal to electrical conversion efficiency in different TEGs based on catalytic combustion are shown. The TEG presented in this work represents an improvement in the conversion efficiency compared to other published works.

 Table 2. Comparison of the TE power generation obtained in this work with those of other published works.

source	fuel	overall power produced, W	conversion efficiency %
Federici, 2006 ^[27]	propane	0.45	0.42
Norton, 2004 ^[5]	hydrogen		1.08
Marton, 2011 ^[47]	butane	5.82	2.53
Yoshida, 2006 ^[46]	hydrogen	0.18	2.8
This work	propane	9.86	2.85

 Future developments of the TEG device presented in this work will include an upgrade of the ignition system with inlet gases preheated through exhaust gases recycling, and preheated inlet gases replacing the hydrogen-assisted ignition.

Concluding Remarks

 A novel premixed catalytic meso-scale combustor fueled with propane/air was developed to be coupled with a thermo-electric device for portable electric applications. Due to the need to use commercially-318 available thermoelectric devices, the limitation of temperature at 250° C was a stringent requirement to match. Therefore, the proper mass flow rate value was found inside the stability limits which produced reasonable values of temperature on the combustor surfaces. In order to investigate the temperature distribution on the combustor surfaces, temperature measurements were carried out by using an IR camera. A uniform distribution on both sides was obtained, assuring thermo-electric conversion optimization.

 Quantitative analysis of the gas-species concentration of the exhaust was performed by FT-IR measurements. From these measurements, the propane conversion efficiency values were derived in the different experimental conditions under study. It was found that reasonable high efficiency of about 96% was obtained at the stoichiometric condition.

 Considering the catalytic pellets degradation during combustion, a change of the distribution of Pt on the alumina surface was observed, resulting in bigger and more complex structures. No significant effects of the coating degradation on the overall combustor performance were observed after 200 h. These results suggest that the combustor proposed is suitable for thermo-electric conversion application. The controlled combustion conditions and the low consumption of the Pt layer suggest a longer expected lifetime for a catalytic combustor in comparison to a traditional combustor. This aspect couples the thermoelectric device advantage in terms of long life without maintenance: the generator has no moving parts and demonstrates long-lasting operative stability.

 The catalytic combustor was integrated with TE modules to produce 9.86 W of electrical power with a thermal to electrical conversion efficiency of 2.85%. The proposed device represents a notable improvement in portable-scale electrical power production from hydrocarbon fuels, with an increase in the conversion efficiency compared to other published works.

 Future perspectives include reducing the system scale, and exploiting the hot gases recirculation in order to reduce the heat losses and further increase the thermal to electrical conversion efficiency. The downscale of the dimension is going to focus on maintaning the highest possible level of power production but with a specific care for the voltage level obtained, in order to ensure both ranges are suitable for power supplying of portable electronic devices.

Acknowledgements

 The authors would like to acknowledge the financial support for the project INTEGRATE in the framework of CNR-Regione Lombardia program, the technical assistance of Mr Fantin, and Ms. Paula Albin Reynolds for editing contribution.

References

- [1] Vican, J. G. B. F., Gajdeczko, B. F., Dryer, F. L., Milius, D. L., Aksay, I. A., and Yetter, R. A., "Development of a microreactor as a thermal source for microelectromechanical systems power
- 354 generation", *Proceedings of the Combustion Institute*, 29(1): 909-916 (2002).
355 [2] Maruta, K., "Micro and mesoscale combustion", *Proceedings of the C* [2] Maruta, K., "Micro and mesoscale combustion", *Proceedings of the Combustion Institute*, *33*(1), 125-150 **356** (2011).
357 [3]
- 357 [3] Yang, W. M., Chou, S. K., Shu, C., Xue, H., Li, Z. W., Li, D. T., and Pan, J. F., "Microscale combustion research for application to micro thermophotovoltaic systems", *Energy Conversion and Management*, 44(16), research for application to micro thermophotovoltaic systems", *Energy Conversion and Management*, *44*(16), 2625-2634 (2003).
[4] Fernandez
- [4] Fernandez-Pello, A.C., "Micropower Generation Using Combustion: Issues and Approaches", *Proceedings of the Combustion Institute*, 29: 883-899 (2002).
- [5] Norton, D. G., Voit, K. W., Brüggemann, T., Vlachos, D. G., and Wetzel, E. D. "Portable power generation via integrated catalytic microcombustion-thermoelectric devices", *in 24th Army Science Conference, Orlando, FL,* 2004.
- [6] Hua, J., Wu, M., and Kumar, K., "Numerical simulation of the combustion of hydrogen–air mixture in
- micro-scaled chambers Part II: CFD analysis for a micro-combustor", *Chemical engineering science*, *60*(13),
- 3507-3515 (2005).Patil, A. S., Dubois, T. G., Sifer, N., Bostic, E., Gardner, K., Quah, M., & Bolton, C., "Portable
- fuel cell systems for America's army: technology transition to the field", *Journal of Power Sources*, *136*(2), 220-
- 225 (2004).
- 370 [7] Yadav, S., Sharma, P., Yamasani, P., Minaev, S., and Kumar, S., "A prototype micro-thermoelectric power generator for micro-electromechanical systems", *Applied Physics Letters*, 104(12), 123903 (2014).
- 371 power generator for micro-electromechanical systems", *Applied Physics Letters*, 104(12), 123903 (2014).
372 [8] Dunn-Rankin, D., Leal, E.M., Walther, D.C., "Personal power systems", *Progress in Ener*
- [8] Dunn-Rankin, D., Leal, E.M.,Walther, D.C., "Personal power systems", *Progress in Energy and Combustion Science* 31: 422–465 (2005).
- [9] Choi, W., Kwon, S., and Dong Shin, H., "Combustion characteristics of hydrogen–air premixed gas in a sub-millimeter scale catalytic combustor", *International Journal of Hydrogen Energy*, *33*(9), 2400-2408 (2008).
- [10] Norton, D.G., Wetzel, E.D., and Vlachos, D.G., "Fabrication of single-channel catalytic microburners:
- effect of confinement on the oxidation of hydrogen/air mixtures", *Industrial & Engineering Chemistry Research* 378 43, 4833-4840 (2004).
379 [11] Wierzbicki, T.
- 379 [11] Wierzbicki, T. A., Lee, I. C., and Gupta, A. K. "Combustion of propane with Pt and Rh catalysts in a meso-scale heat recirculating combustor", *Applied Energy*, 130, 350-356 (2014). meso-scale heat recirculating combustor", *Applied Energy*, *130*, 350-356 (2014).
- [12] Pattekar, A.V., Kothare, M.V., "A radial microfluidic fuel processor", *Journal of Power Sources* 147: 116–127 (2005).
- [13] Norton, D.G., and Vlachos, D.G., "A CFD study of propane/air microflame stability". *Combustion and Flame* 138, 97–107 (2004).
- [14] Kaisare, N.S., Vlachos, D.G., "Optimal reactor dimensions for homogeneous combustion in small channels", *Catalysis Today* 120: 96–106 (2007).
- 387 [15] Miesse, C. M., Masel, R. I., Jensen, C. D., Shannon, M. A., and Short, M., "Submillimeter-scale combustion". AIChE Journal, 50 12: 3206-3214 (2004). 388 combustion". *AIChE Journal*, 50 12: 3206-3214 (2004).
389 [16] Kaisare, N.S., Deshmukh, S.R., and Vlach
- 389 [16] Kaisare, N.S., Deshmukh, S.R., and Vlachos, D.G., "Stability and performance of catalystic microreactors: Simulations of propane catalytic combustion on Pt", Chemical Engineering Science 63, 1098-1116 microreactors: Simulations of propane catalytic combustion on Pt", *Chemical Engineering Science* 63, 1098-1116 $(2008).$
- [17] Norton, D.G., Wetzel, E.D., and Vlachos, D.G., "Thermal management in catalytic microreactors", *Industrial & Engineering Chemistry Research* 45: 76–84 (2006).
- [18] Ouyang, X., Bednarova, L., Besser, R. S., and Ho, P., "Preferential oxidation (PrOx) in a thin‐film catalytic microreactor: Advantages and limitations", *AIChE journal*, *51*(6), 1758-1772 (2005).
- [19] Rebrov, E. V., De Croon, M. H. J. M., and Schouten, J. C., "A kinetic study of ammonia oxidation on a Pt catalyst in the explosive region in a microstructured reactor/heat-exchanger", *Chemical Engineering Research and Design*, *81*(7), 744-752 (2003).
- [20] Deshmukh, S.R., and Vlachos, D.G., "A reduced mechanism for one-step rate expressions for catalytic 400 combustion of small alkanes on noble metals", *Combustion and Flame* 149: 366–383 (2007).
401 [21] Saracco, G., Veldsink, J. W., Versteeg, G. F., and van Swaaij, W. P., "Catalytic con
- 401 [21] Saracco, G., Veldsink, J. W., Versteeg, G. F., and van Swaaij, W. P., "Catalytic combustion of propane
402 in a membrane reactor with separate feed of reactants—II. Operation in presence of trans-membrane pressure in a membrane reactor with separate feed of reactants—II. Operation in presence of trans-membrane pressure
- gradients", *Chemical engineering science*, *50*(17), 2833-2841 (1995). 404 [22] Deshmukh, S. R., Mhadeshwar, A. B., Lebedeva, M. I., and Vlachos, D. G. "From density functional theory to microchemical device homogenization: model prediction of hydrogen production for portable fuel cells", theory to microchemical device homogenization: model prediction of hydrogen production for portable fuel cells",
- 106 *International Journal for Multiscale Computational Engineering*, 2(2) (2004).

107 [23] Ganley, J. C., Seebauer, E. G., and Masel, R. I., "Development of a 407 [23] Ganley, J. C., Seebauer, E. G., and Masel, R. I., "Development of a microreactor for the production of hydrogen from ammonia", *Journal of Power Sources*, 137(1), 53-61 (2004). hydrogen from ammonia", *Journal of Power Sources*, *137*(1), 53-61 (2004).
- 409 [24] Deshmukh, S. R., and Vlachos, D. G. "Effect of flow configuration on the operation of coupled combustor/reformer microdevices for hydrogen production", *Chemical Engineering Science*, 60(21), 5718-5728 combustor/reformer microdevices for hydrogen production", *Chemical Engineering Science*, *60*(21), 5718-5728 $(2005).$
- [25] Kolios, G., Glöckler, B., Gritsch, A., Morillo, A., and Eigenberger, G., "Heat‐Integrated Reactor Concepts for Hydrogen Production by Methane Steam Reforming", *Fuel Cells*, *5*(1), 52-65 (2005).
- [26] Norton, D., Deshmukh, S. R., Wetzel, E. D., and Vlachos, D. G., "Downsizing chemical processes for
- portable hydrogen production", *ACS symposium series* (Vol. 914, pp. 179-193). Oxford University Press (2005).
- [27] Federici, J. A, Norton, D. G., Bruggeman, T., and Voit, K.W., "Catalytic Microcombustor with integrated thermoelectric elemenst for portable production", *Journal of Power Sources* 161, 1469-1478 (2006).
- [28] Ahn, J., Eastwood, C., Sitzki, L., and Ronney, P. D., "Gas-phase and catalytic combustion in heat-recirculating burners", *Proceedings of the Combustion Institute*, *30*(2), 2463-2472 (2005).
- 420 [29] Zhang, S., Yuan, X. Z., Hin, J. N. C., Wang, H., Friedrich, K. A., and Schulze, M., "A review of platinum-
421 based catalyst layer degradation in proton exchange membrane fuel cells", *Journal of Power Sources* 1 based catalyst layer degradation in proton exchange membrane fuel cells", *Journal of Power Sources* 194.2 (2009): 588-600.
- [30] Wu, M., Yetter, R.A., and Yang, V., "Combustion in meso-scale vortex combustors: experimental characterization", 42nd AIAA Aerospace Sciences Meeting and Exhibit, 5-8 Jan. 2004, Reno, Nevada. AIAA
- 425 2004-980 (2004).
426 [31] Wierzbic 426 [31] Wierzbicki, T.A., Lee, I.C., and Gupta, A.K.. "Combustion of propane with Pt and Rh catalysts in a meso-
427 scale heat recirculating combustor." Applied Energy 130 (2014): 350-356.
- scale heat recirculating combustor." *Applied Energy* 130 (2014): 350-356. [32] Neyestanaki, A. K., Kumar, N., and Lindfors, L-E. "Catalytic combustion of propane and natural gas over Cu and Pd modified ZSM zeolite catalysts."*Applied Catalysis B: Environmental* 7.1 (1995): 95-111.
- 430 [33] Vijayan, V., and Gupta, A.K., "Combustion and Heat Transfer at Meso-scale with thermal recuperation", 431 *J. Applied Energy*, Vol. 87, No. 8, August 2010, pp. 2628-2639.
- *J. Applied Energy*, Vol. 87, No. 8, August 2010, pp. 2628-2639.
- [34] Vijayan, V., and Gupta, A.K., "Flame Dynamics of a Meso-scale Heat Recirculating Combustor", *J.*
- *Applied Energy*, Vol. 87, No. 12, December 2010, pp. 3718-3728.
- [35] Vijayan, V., and Gupta, A.K., "Thermal Performance of a Meso scale Liquid Fuel Combustor", *J. Applied Energy*, Vol. 88, issue 7, 2011, pp. 2335-2343.
- [36] Shirsat, V, and Gupta, A.K., "Performance Characteristics of Methanol and Kerosene Fuelled Meso-Scale Heat Recirculating Combustors", *J. Applied Energy*, Volume 88, 2011, pp. 5069-5082.
- [37] Yazawa, Y., Takagi, N., Yoshida, H., Komai, S. I., Satsuma, A., Tanaka, T., Yoshida, S., and Hattori, T.,
- "The support effect on propane combustion over platinum catalyst: control of the oxidation-resistance of platinum by the acid strength of support materials." *Applied Catalysis A: General* 233.1 (2002): 103-112.
- 441 [38] González-Velasco, J. R., Botas, J. A., Ferret, R., Pilar González-Marcos, M., Marc, J. L., and Gutiérrez-
442 Ortiz, M. A., "Thermal aging of Pd/Pt/Rh automotive catalysts under a cycled oxidizing-reducing Ortiz, M. A., "Thermal aging of Pd/Pt/Rh automotive catalysts under a cycled oxidizing–reducing
- environment", *Catalysis today* 59.3 (2000): 395-402.
- 444 [39] Mayrhofer, K. J., Meier, J. C., Ashton, S. J., Wiberg, G. K., Kraus, F., Hanzlik, M., and Arenz, M., "Fuel cell catalyst degradation on the nanoscale", *Electrochemistry Communications* 10.8 (2008): 1144-1147. 445 cell catalyst degradation on the nanoscale", *Electrochemistry Communications* 10.8 (2008): 1144-1147.
446 [40] Hanst, P. L., "Infrared spectroscopy and infrared lasers in air pollution research and monitoring"
- [40] Hanst, P. L., "Infrared spectroscopy and infrared lasers in air pollution research and monitoring", *Applied Spectroscopy*, *24*(2), 161-174 (1970).
- 448 [41] Baum, M. M., Kiyomiya, E. S., Kumar, S., Lappas, A. M., Kapinus, V. A., and Lord, H. C., 449
449 "Multicomponent remote sensing of vehicle exhaust by dispersive absorption spectroscopy. 2. Direct on-road 449 "Multicomponent remote sensing of vehicle exhaust by dispersive absorption spectroscopy. 2. Direct on-road 450 ammonia measurements". *Environmental science & technology*. 35(18). 3735-3741 (2001). 450 ammonia measurements", *Environmental science & technology*, 35(18), 3735-3741 (2001).
451 [42] Aranguren, P., Astrain, D., Rodríguez, A., and Martínez, A. "Experimental"
- [42] Aranguren, P., Astrain, D., Rodríguez, A., and Martínez, A. "Experimental investigation of the applicability of a thermoelectric generator to recover waste heat from a combustion chamber." *Applied Energy* 152 $(2015): 121-130.$
- [43] Chou, S. K., Yang, W.M., Chua, K.J., Li, J., and Zhang, K.L. "Development of micro power generators–a review." *Applied Energy* 88.1 (2011): 1-16.
- [44] Kinsella, C. E., O'Shaughnessy, S.M., Deasy, M.J., Duffy, M., and Robinson, A.J. "Battery charging considerations in small scale electricity generation from a thermoelectric module." *Applied Energy* 114 (2014): 80-90.
- 459 [45] Xiao, H., Qiu, K., Gou, X., and Ou, Q. "A flameless catalytic combustion-based thermoelectric generator 460 for powering electronic instruments on gas pipelines." Applied Energy 112 (2013): 1161-1165. for powering electronic instruments on gas pipelines." *Applied Energy* 112 (2013): 1161-1165.
- Yoshida, K., Tanaka, S., Tomonari, S., Satoh, D., and Esashi, M., "High-energy density miniature thermoelectric generator using catalytic combustion". *Microelectromechanical Systems, Journal of*, *15*(1), 195-
- 463 203 (2006).
464 [47] Ma 464 [47] Marton, C.H., Haldeman, G.S., and Jensen, K.F., "Portable thermoelectric power generator based on a
465 microfabricated silicon combustor with low resistance to flow". Industrial & Engineering Chemistry microfabricated silicon combustor with low resistance to flow". *Industrial & Engineering Chemistry Research*,*50*(14), 8468-8475 (2011).
- [48] Shirsat, V., and A. K. Gupta. "A review of progress in heat recirculating meso-scale combustors." *Applied Energy* 88.12 (2011): 4294-4309.
- [49] Tolmachoff, Erik D., William Allmon, and C. Mike Waits. "Analysis of a high throughput n-dodecane fueled heterogeneous/homogeneous parallel plate microreactor for portable power conversion." *Applied Energy* 128 (2014): 111-118.
- [50] Vijayan, V., and A. K. Gupta. "Combustion and heat transfer at meso-scale with thermal recuperation." *Applied Energy* 87.8 (2010): 2628-2639.
- [51] Merotto, L., Dondè, R., and De Iuliis, S., "Study of the Performance of a Catalytic Premixed Meso-scale
- Burner", Ninth Mediterranean Combustion Symposium, Rhodes, Greece, 7-11 June 2015.