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Lo Basso, G.; Nastasi, Benedetto; Astiaso Garcia, D.; Cumo, F.

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## How to handle the Hydrogen enriched Natural Gas blends in combustion efficiency measurement procedure of conventional and condensing boilers



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### Gianluigi Lo Basso <sup>a</sup>, Benedetto Nastasi <sup>b, \*</sup>, Davide Astiaso Garcia <sup>a</sup>, Fabrizio Cumo <sup>c</sup>

<sup>a</sup> Department of Astronautics, Electrical and Energy Engineering (DIAEE), Sapienza University of Rome, Via Eudossiana, 18, 00184 Rome, Italy
 <sup>b</sup> Department of Architectural Engineering and Technology (AE+T), TU Delft University of Technology, Julianalaan 134, 2628BL Delft, The Netherlands
 <sup>c</sup> Department of Planning, Design, and Technology of Architecture (DPDTA), Sapienza University of Rome, Via Flaminia 72, 00196 Rome, Italy

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#### ABSTRACT

This paper focused on the hydrogen-methane mixtures (H<sub>2</sub>NG) implications on end-user devices such as boilers, so as to provide a useful tool for maintenance operators. In detail, according to current standards, H<sub>2</sub>NG blends characteristics parameters for boilers combustion efficiency measurement are calculated. Then, the Ostwald chart for each blend is built by the analytical procedure and is plotted. Additionally, the chemical equations as well as the blended gas characteristic values are computed in order to implement them within software library of commercial gas analysers. Indeed, they are commonly based on Ostwald combustion equation for correlating CO, CO<sub>2</sub> and O<sub>2</sub> concentrations. The results can be applied to analyze conventional and widespread domestic boilers fueled with H<sub>2</sub>NG addressing all of the technical implications for their performance certification when they are operating also in condensing mode. Air excess and relative humidity are chosen as variables to evaluate their effects on boilers performance. The oxygen concentration ranges from 0% vol. up to 15% vol. The specific heat values drop nonlinearly down for each mixture, showing a maximum reduction equal to 9.825%, for H<sub>2</sub>NG@30%. A maximum Energy Fraction of Condensation (EFC) enhancement of 0.9% points is noticed for H<sub>2</sub>NG@30% vol. While, the highest EFC gain, 4.8% points, occurred at relative humidity of 90% compared to the assumed reference values for calculations.

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#### 1. Introduction

Nowadays, hydrogen offers good opportunities to decarbonize the current economies and energy supplies. Even though it is the most present chemical element in nature, it has to be produced for energy end-use. Additionally, it represents a real carbon-free energy carrier but, the technologies to produce it cause a carbon footprint not alike to zero. Among those options, the hydrogen production from Renewable Energy Sources (RES) is the less polluting one. Since several EU countries have implemented in the last years energy policies and incentives to promote and fund the widespread deployment of renewables in national energy mixes, Grid security, safety and balancing issues derive from renewables

\* Corresponding author. E-mail address: benedetto.nastasi@outlook.com (B. Nastasi). URL: http://it.linkedin.com/in/benedettonastasi intermittency. RES capacity firming could be feasibly solved by energy storage application such as the so-called Power-to-Gas (P2G) and Power-to-Liquid (P2L) [1]. Basically, the electricity excess could be converted in gaseous or liquid fuels such as pure hydrogen, its mixtures and its further synthesis with carbon dioxide to generate electro-fuels, e.g. synthetic methane and methanol by Sabatier reaction, or synthetic diesel by Fischer-Tropsch process [2–4]. Pure hydrogen entails critical issues related to its storage technologies owing to the very low molecular weight as well as their location [5]. Moreover, high energy consumption for compressing and cooling it along with expensive facilities are needed to handle hydrogen. A sustainable compromise is the Hydrogen (H<sub>2</sub>) use combined with fossil sources [6], such as Natural Gas (NG), to create more environmentally-friendly fuels [7–9]. Indeed, recent studies on hydrogen mixtures application to both internal combustion engines and atmospheric burners demonstrated that the CO and CO<sub>2</sub>values produced from Hydrogen enriched Natural Gas blends (H<sub>2</sub>NG) burning are lower than any other gaseous fuel



[10,11]. In this way, ready large-storage facilities, built for fossil fuel distribution, could be coupled with a distributed hydrogen production by means of its direct injection in pipelines [12]. Indeed, several gaseous mixtures are already classified by their thermophysical properties and combustion behaviour as reported in Table 1.

The feasibility of using  $H_2NG$  is confirmed by the acceptable standard composition of established NG end-users, e.g. cooker and boilers. Any devices designed to burn NG has to be tuned also to use listed gaseous fuel mixtures complying with ISO 13686:2013 [13], specified in Table 2.

Referring to this data, H<sub>2</sub>NG belong to this group, so as to be immediately used in well-proven energy systems. Their integration into existing Gas Grid without incurring excessive costs and technical constraints were deeply investigated by several research projects [14–17]. Given that a proven compatibility is well-known in literature, the focus of new research is on end-user devices. Among the stationary applications for power generation, the combined heat and power production (CHP) was studied by different authors [18–21], whereas the H<sub>2</sub>NG use in boilers is poorly analyzed. Not hwithstanding, a number of studies investigated on burners typologies, features and performance in terms of  $NO_x$  and CO emissions reduction [22–24], energy saving [25], combustion stability [26], safety issues [27] and foreseeable design and development of technological components [28,29]. Yet, only one research activity is related to boiler efficiency evaluation [30] but, it is even not the main subject of that publication.

The authors, based on their experience in research related to  $H_2NG$  application, identified a gap in literature about the blends integration in the current standards and regulations for conventional and condensing boilers. In details, this study addresses the practical aspects of emissions measurements and the subsequent procedure to assess efficiency of boiler fuelled with  $H_2NG$  mixtures, faced by technicians and maintenance operators in periodic checks. So, under the hypothesis of a forthcoming hydrogen spreading, the analytical method to immediately upgrade the gas analyserssoftwarelibrarywas developed so as to update standards as well.

Since many research activities dealing with hydrogen firing and cofiring were carried out on special applications such as lab-scale furnace [31], research engine for detonation tests [32], heavy-duty engines [33], commercial CHP [34] and cutting-edge catalytic combustors [35], the authors believe that the added value of the present work consists of providing a new set of values and charts related to those new eco-fuels; moreover, the overview and discussion on technical implications and potential energy gains deriving from hydrogen use especially in condensing boilers, could be considered valuable for filling the gap in literature and for contributing to promote the hydrogen exploitation in the short term as well.

#### 2. Objectives

Since the hydrogen can be considered as an alternative and environmentally-friendly fuel, its employment in automotive sector, in stationary power generation systems such as CHP, and in

Table 1Standard compositions of Natural Gas complying with ISO 13686:2013.

Gas name	Description	Composition
G20	Pure methane	100% CH <sub>4</sub>
G21	Limit gas for incomplete combustion	$87\% \text{ CH}_4 + 13\% \text{ C}_3 \text{H}_8$
G22	Limit gas for backfire	$65\% \text{ CH}_4 + 35\% \text{ H}_2$
G23	Limit gas for misfire	92.5% $\rm CH_4 + 7.5\%~N_2$

#### Table 2

Standard compositions of Hydrogen enriched Natural Gas mixtures complying with ISO 13686:2013.

Gas name	Composition
G110	$26\% \ \text{CH}_4 + 50\% \ \text{H}_2 + 24\% \ \text{N}_2$
G112	17% CH <sub>4</sub> +59% H <sub>2</sub> + 24% N <sub>2</sub>
G120	32% CH <sub>4</sub> +47% H <sub>2</sub> + 21% N <sub>2</sub>
G222	$77\% \ CH_4 + 23\% \ H_2$

household application as well, was largely investigated [36]. Due to its unique properties - i.e. low ignition energy and wide flammability range - the pure hydrogen use showed several drawbacks from a safety point of view. For instance, the self-ignition of highpressure hydrogen release is a crucial issue as well as the main barrier for the hydrogen deployment, especially in current domestic devices. Nevertheless, when it is blended with other gaseous fuels, it is less dangerous [37,38]. Indeed, the methane doping effect on self-ignition process was widely demonstrated and it is very strong. So, accounting for the use of pressurised hydrogen, it is possible to increase the safety level by doping the methane to hydrogen [39,40]. Having said, the methane enrichment by hydrogen up to 30% by volume mitigates largely the hydrogen dangerousness and results suitable for burning within other domestic appliances such as boilers.

Hence, the authors identified two research questions to be answered by this study:

- 1. Having observed the beneficial effects on Internal Combustion Engines, what would be the theoretical gains coming from H2NG blends use in conventional and condensing boilers?
- 2. Since current regulations and technical specifications do not account for those blends, how to update the correlation for carbon monoxide and dioxide measurements taken by commercial gas analyser so as to evaluate the combustion efficiency?

The aim of this paper is to identify the  $H_2NG$  blends characteristic parameters according to the current standards and regulations for boilers combustion efficiency measurement. Thus, the hydrogen addition effects on condensing boilers, owing to the higher water content in exhaust gases, are presented and discussed, highlighting the potential combustion efficiency gains.

Moreover, the Ostwald charts for each mixture are analytically built so as to provide, on one hand a graphical tool, on the other hand, the chemical equation associated to CO,  $CO_2$  and  $O_2$  concentrations within dry exhaust gas for a further implementation in the commercial gas analyzers software. In the end, an user-friendly graphical and analytical procedure is developed in order to take into account how the air excess set up during combustion processes as well as the air Relative Humidity (RH) affect both thermal and condensation efficiency.

#### 3. H<sub>2</sub>NG Ostwald charts

It is well known that in thermal engineering, four combustion typologies can occur during burners operation. Specifically, stoichiometric and complete combustion (i.e. relative equivalence ratio equal to 1) can be considered as a theoretical reference for comparing the expected energy-environmental performance to the actual ones deriving from on-field measurements. Thereafter, the lean burning conditions (i.e. relative equivalent ratio higher than 1) entail an air excess in order to ensure the complete hydrocarbons oxidation as much as possible and to reduce the NO<sub>x</sub> formation owing to the flames temperature above 1100 °C. Additionally, even

if the air excess set up leads to better environmental performance, it generally implies a combustion efficiency reduction. So, specific adjustments are required to optimize the energy conversion process [41]. Rich combustion (i.e. relative equivalence ratio lower than 1) denotes a chemical reaction occurring with air amount shortage compared to the stoichiometric one, and it is a typical operating condition for internal combustion engines (ICEs) in the automotive sector. Finally, incomplete combustion is possible where high gradients of temperature, caused by flames development, rise within a closed and cooled domain, resulting mainly in carbon monoxide and unburned hydrocarbons (HC) production as well. Actually, when a burner operates, lean and incomplete combustion process is set up very often so as to optimize the heat exchange and to reduce pollutants emission. In that case, nitrogen or its compounds, residual oxygen, carbon dioxide, carbon oxide, unburned hydrocarbons and water vapour are the chemical components of the exhaust gas. Then, under the hypotheses of neglecting HC and condensing out the water vapour, oxygen concentration along with the carbon dioxide and oxide ones, related to a specific fuel burning, can be correlated by chemical equations and mass balances. Those correlations can be outlined in a graphical way by means of the so-called Ostwald charts. Up to date, those correlations are still used by gas analysers to verify the limit values of boilers energy performance complying with current regulations and standards.

Having said, in the Appendix, the analytical procedure for Ostwald charts construction related to  $H_2NG$  blends with varying the added %  $H_2$  vol., is presented.

Having manipulating Equations A.16, A.17, the so called Ostwald equation for combustion was deduced:

$$\frac{[CO_2]}{[CO_2]_{th}} + \frac{[CO]}{[CO]_{th}} + \frac{[O_2]}{m} = 1$$
(1)

Thus, in Table 3 the characteristic concentration values for both CO and  $CO_2$ to set up the gas analyser with varying the hydrogen volumetric fraction were given:

From an analytical point of view, this equation can be represented on a Cartesian chart (the x-axis and the y-axis are  $[CO_2]$ ;  $[O_2]$ respectively), by means of a parallel lines beam using carbon monoxide concentration [CO] as the parametric value.

The intersection point coordinates with reference axis can be calculated as follows:

$$([O_2]; \mathbf{0}) = \left[ m \left( 1 - \frac{[CO]}{[CO]_{th}} \right); \mathbf{0} \right]$$
(2)

$$(0; [CO_2]) = \left[0; [CO_2]_{th} \left(1 - \frac{[CO]}{[CO]_{th}}\right)\right]$$
(3)

In the Ostwald charts for fuels, the air excess curves with constant value are superimposed. Those curves are useful once a measurement instrument for relative equivalence ratio or percentage air excess assessment is available. In that case, the oxygen content and carbon compounds concentration can be deduced immediately by a graphical way, or vice versa.

The percentage air excess can be defined as:

$$e = \frac{V_{air} - V_{air,st}}{V_{air,st}} = \frac{V_{air\ excess}}{V_{air,st}}$$
(4)

Thus, assuming:

$$C = C_{CO} + C_{CO_2} = 12V_{exh,dry,TOT} ([CO_2]_{act} + [CO]_{act})$$

$$(5)$$

it is possible to point out that C results as the summed value of two different terms: the former is related to the carbon mass reacting for carbon dioxide formation; the latter represents the carbon mass which contributes to carbon monoxide formation.

Consequently, a more sophisticated expression for percentage air excess is calculated:

$$e = \frac{\left(V_{air\ excess} - \frac{[CO]_{act}V_{exh.dry,TOT}}{2m}\right)(1-m)[CO_2]_{th}}{V_{exh.dry,TOT}([CO_2]_{act} + [CO]_{act})(1-[CO_2]_{th})}$$
(6)

$$e = \frac{\left(\frac{[O_2]}{m} - \frac{[CO]_{act}}{2m}\right)(1 - m)[CO_2]_{th}}{\left([CO_2]_{act} + [CO]_{act}\right)\left(1 - [CO_2]_{th}\right)}$$
(7)

Substituting Equation 7in the Ostwald equation for combustion, the percentage air excess curves are determined as well as their axis intersections:

$$\left(0; \frac{\left[\frac{(1-m)}{2m}[CO_2]_{th}[CO]_{th} + e(1 - [CO_2]_{th})[CO]_{th}\right]}{\left[\frac{(1-m)}{m}[CO_2]_{th}\left(1 + \frac{[CO]_{th}}{2m}\right) + \frac{e}{m}(1 - [CO_2]_{th})[CO]_{th}\right]}\right)$$
(8)

$$\left(\frac{\left[\frac{-(1-m)}{2m}[CO_2]_{th}[CO]_{th} + e(1-[CO_2]_{th})[CO]_{th}\right]}{\left[e(1-[CO_2]_{th})\left(1+\frac{[CO]_{th}}{[CO_2]_{th}}\right) - \frac{[CO]_{th}(1-m)}{2m}\right]};0\right)$$
(9)

Finally, two Ostwald charts for H<sub>2</sub>NG blends have been reported on the basis of previous equations, referring to the hydrogen content equal to 0% and 30% of hydrogen, by volume. It is important to point out that, even if maximum values for CO in boiler emissions allowed by regulation are tiny fraction of % (i.e. 80 ppm or 100 mg/ Nm<sup>3</sup> for normalized measurement of O<sub>2</sub> @3%vol.), all typical CO values up to the characteristic ones to set up gas analyser are depicted in Figs. 1 and 2 for completeness. This is the reason why the authors provided the entire graphs. In detail, the red diamond points represent the y-axis and x-axis intersections of percentage air excess e when it is equal to zero and the coordinates value is superimposed on the chart. It is important to point out that the xaxis intersection describes the complete and stoichiometric combustion conditions of H<sub>2</sub>NG blends showing the characteristic CO2 concentration in dry exhaust gas; while the y-axis one describes a stoichiometric combustion characterised by a high incompleteness degree. In addition, the black dashed lines represent the general coordinates of a measurement point. It is noteworthy that all of measurement points must be either encapsulated within the area limited by the boundary line of Ostwald triangle or has to belong to that limit line. Whether a measurement point was represented outside the triangle it will be a not realistic condition and it will indicate a potential probes malfunctioning.

Та	bl	e	3

Characteristic CO and CO <sub>2</sub> concentrations within dry exhaust gases produced by $H_2N$	AG blends to set up the gas analyser
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f <sub>H2</sub> [% vol.]	0%	5%	10%	15%	20%	25%	30%
[CO <sub>2</sub> ] <sub>th</sub> [% vol.]	11.669%	11.535%	11.390%	11.232%	11.059%	10.869%	10.661%
[CO] <sub>th</sub> [% vol.]	14.977%	14.757%	14.519%	14.263%	13.986%	13.684%	13.355%



Fig. 1. Ostwad chart for H<sub>2</sub>NG @ 0% of hydrogen fraction.

#### 4. Discussion on boilers efficiency

The fuel energy content is converted partially into useful heat by boilers, owing to the fact that energy losses occur during their operation caused by exhaust gases discharge temperature, blowdown, and heat radiation throughout the boiler case surfaces. The boilers efficiency is usually rated based on combustion efficiency, thermal efficiency, and overall efficiency.

The first one indicates the burner ability to combust fuel along with the boiler ability to absorb the generated heat. Additionally, the unburnt fuel amount and air excess in the exhaust gas are used to estimate the burner combustion efficiency. The thermal efficiency is strictly connected to the heat exchange within the boiler, i.e. it indicates how well the heat exchanger transfers heat from the combustion process to water. It does not account for the conduction and convection losses from the boiler external surfaces. Finally, the overall boiler efficiency measures how well the boiler is able to convert the heat input from the combustion process to the useful one yielded tothe working fluids. This latter requires for its determination direct and accurate measurements from both output and input sides. In detail, the water flow rate, the fuel flow rate and the water temperature difference have to be registered by dedicated instruments characterized by very small relative error and high accuracy. Those ones are usually expensive and they would be not cost effective for any nonindustrial applications.

Referring to Fig. 3, the simplified energy balance of boiler is reported below (Eq. (10)), once the unburned hydrocarbons energy loss has been neglected:

$$P_{fuel} = P_{useful} + P_{loss, sens} + P_{loss, radiative}$$
(10)

Consequently, the overall efficiency can be calculated by Equation (11):

$$\eta_{ov} = \frac{P_{useful}}{P_{fuel}} \tag{11}$$

Since that efficiency can be experimentally evaluated by keeping under control all of operating parameters, its values are usually determined in laboratory by manufacturers and reported in product data sheets for rated and minimum loads. When a boiler runs in actual conditions for a long time within the heating plant, periodic checks are required in order to verify its wear state, combustion quality and the allowed limit of pollutants emissions. It is noteworthy that efficiency testing helps the end-user to find out how far the boilers efficiency drifts away from the best values, allowing firstly to optimize the fuel burning and, secondly, to evaluate the onset of heat exchanger fouling. For these reasons, several regulations and standards (e.g. UNI 10389 in Italy) established the combustion efficiency measurement as the expeditious procedure that technicians must follow to certificate the boiler performance. To do so, the so-called indirect method for combustion efficiency determination has to be applied [42], consisting of the sensible heat loss assessment in accordance with Equation (12), by using temperature probes and gas analysers.

$$\eta_c = 1 - \frac{P_{loss,sens}}{P_{fuel}} \tag{12}$$

It is remarkable that combustion efficiency results always higher than the overall one due to the radiative/convective heat losses neglecting, and it should not be used as the reference factor for



Fig. 2. Ostwad chart for H<sub>2</sub>NG @ 30% of hydrogen fraction.

economic evaluations.

As regards the condensing boilers, the UNI 10389 standard defined the combustion efficiency by Equation (13):

$$\eta_c = 1 - \frac{P_{loss,sens}}{P_{fuel}} + EFC \tag{13}$$

Where:

$$EFC = \frac{P_{latent}}{P_{fuel}}$$
(14)

It indicates the latent heat fraction deriving from water vapour condensation related to boiler input energy. Once the water dew point temperature along with the exhaust gas temperature to the stack are known, it is possible to calculate the condensed out water mass, the effective recovered latent heat and the Energy Fraction of Condensation (EFC) factor value, thereafter. As the water dew point depends on vapour molar fraction in exhaust gases and on fuel hydrogen to carbon ratio, several correlations between flue temperature and water mass content have to be implemented for each fuel. Having said, the hydrogen enrichment effects on combustion efficiency measurement, coefficients and correlations as well, are presented in the next sections.

#### 4.1. H<sub>2</sub>NG effects on conventional boilers

In this section, the influence of the hydrogen enrichment on technical parameters for boilers performance certification as well as the current procedure adjustment is presented.

Referring to Equation (12), the sensible heat loss to input

thermal power ratio reads as:

$$\frac{P_{loss,sens}}{P_{fuel}} = \frac{m_{exh} \cdot c_{p,exh}}{m_{fuel} \cdot LHV} \cdot \Delta T$$
(15)

Where:

$$\frac{m_{exh}}{m_{fuel}} = \alpha_{st} + 1 \tag{16}$$

Here,  $\alpha_{st}$  denotes the stoichiometric air to fuel ratio by mass and, when a lean burn is considered, the relative equivalence ratio is defined as:



Fig. 3. Boiler simplified energy balance.

$$\lambda = \frac{\alpha}{\alpha_{st}} \tag{17}$$

As a consequence, the general combustion reaction for H<sub>2</sub>NG blends, as a function of both H<sub>2</sub>volumetric fraction and relative equivalence ratio, is reported below:

$$(1 - f_{H2}) \cdot CH_4 + f_{H2} \cdot H_2 + \lambda \cdot \left[ 2 \cdot (1 - f_{H2}) + \frac{f_{H2}}{2} \right] \cdot (O_2 + 3.7846N_2)$$
  

$$\rightarrow (1 - f_{H2}) \cdot CO_2 + (2 - f_{H2}) \cdot H_2O$$
  

$$+ \left[ 2 \cdot (1 - f_{H2}) + \frac{f_{H2}}{2} \right] \cdot \left[ (\lambda - 1) \cdot O_2 + \lambda \cdot 3.7846N_2 \right]$$
(18)

Thereafter, manipulating Equations (15) and (18), the percentage sensible heat loss is dependent on actual oxygen concentration to the stack, on stoichiometric air to fuel ratio by volume, on the exhaust gas specific heat, on fuel relative density and on its Lower Heating Value (LHV), as reported in Equation (19).

$$\frac{P_{loss,sens}}{P_{fuel}} = \left(\frac{20.9}{20.9 - O_2} \cdot R_d \cdot \alpha_{st,vol} \cdot + 1\right) \cdot c_{p,exh} \cdot \frac{\Delta T}{LHV}$$
(19)

Moreover, it is possible to define the following parameters:

$$R_d \cdot \alpha_{st,vol} = \frac{\rho_{air,st}}{\rho_{fuel}} \cdot \frac{V_{air,st}}{V_{fuel}}$$
(20)

$$K_1 = R_d \cdot \alpha_{st,vol} \cdot 20.9 \cdot \frac{c_{p,exh}}{LHV}$$
(21)

$$K_2 = \frac{c_{p,exh}}{LHV} \tag{22}$$

The percentage sensible heat loss to the stack can be calculated easily by Equation (23), when the K-coefficients are given for each hydrogen-natural gas mixture.

$$\frac{P_{loss,sens}}{P_{fuel}} = \left(\frac{K_1}{20.9 - O_2} + K_2\right) \cdot \Delta T \tag{23}$$

In Table 4, the calculation parameters related to the  $H_2NG$  blends are reported. Those values are referred to an oxygen volumetric content equal to 4%, i.e. a relative equivalence ratio of 1.237. This latter is the typical set-up for conventional boilers so that to assure the complete combustion and to reduce the carbon monoxide emission compared to the stoichiometric burning set up. Moreover, the exhaust gas specific heat was computed having considered an average temperature equal to 50 °C which is defined as the mathematical mean between discharging temperature to the stack and the outdoor environment one.

Whether a gas analyser is equipped with a carbon dioxide probe, the percentage sensible heat loss can be still calculated by measuring $CO_2$  volumetric concentration, directly. Anyway, it is

 Table 4

 Parameters calculation required by Equation (19) with changes in hydrogen fraction.

<i>f</i> <sub>H2</sub> [% vol.]	$\alpha_{st,vol}$	R <sub>d</sub>	c <sub>p,exh</sub> [kJ/kg K]	LHV [kJ/kg]
0%	9.5692	1.72635	1.13713	50,000.00
5%	9.2104	1.80247	1.13899	50,467.32
10%	8.8515	1.88566	1.14101	50,979.45
15%	8.4927	1.97696	1.14320	51,543.17
20%	8.1338	2.07761	1.14559	52,166.67
25%	7.7750	2.18913	1.14820	52,860.00
30%	7.4161	2.31342	1.15106	53,635.59

important to point out that this methodology could lead to great error if it was applied to those gaseous fuels characterized by high  $H_2$ ,  $N_2$ , CO, CO<sub>2</sub> contents which do not take part to combustion process, such as biogas or foundry gas.

On the basis of Ostwald combustion equation, the oxygen concentration as a function of the carbon dioxide one reads as:

$$O_2 = \left(1 - \frac{CO_2}{CO_{2,th}}\right) \cdot 20.9 \tag{24}$$

By substituting Equation (24)in Equation (23), the sensible heat loss is dependent on the theoretical carbon dioxide concentration by volume as well, which is a fuel peculiarity.

$$\frac{P_{loss,sens}}{P_{fuel}} = \left(\frac{CO_{2,th}}{CO_2} \cdot R_d \cdot \alpha_{st,vol} \cdot + 1\right) \cdot c_{p,exh} \cdot \frac{\Delta T}{LHV}$$
(25)

Furthermore, assuming that:

$$K_3 = R_d \cdot \alpha_{st,vol} \cdot CO_{2,th} \cdot \frac{c_{p,exh}}{LHV}$$
(26)

Equation (23) can be rearranged as reported below:

$$\frac{P_{loss,sens}}{P_{fuel}} = \left(\frac{K_3}{CO_2} + K_2\right) \cdot \Delta T \tag{27}$$

Table 5 summarizes the K-coefficients related to all of hydrogen enrichment degrees. From data, it emerges that  $K_1$ ,  $K_2$  and  $K_3$  values diminish as hydrogen volumetric fraction increases. So, with the same recorded exhaust gas temperature the boiler efficiency rises. Thus, all the three K-coefficients depend on specific heat value of the exhaust gas, which is itself linked to the air excess and the reference temperature for calculating it.

4.1.1. Relative equivalence ratio and average temperature influence on specific heat for boiler efficiency calculation

The flue simplified chemical composition associated to  $H_2NG$  mixtures use is considered to calculate the weighted average specific heat values, according to Equation (28) [43].

$$c_{p,exh} = \sum_{j=1}^{N} y_j \cdot c_{p,j}$$
  
=  $y_{N2} \cdot c_{p,N2} + y_{02} \cdot c_{p,02} + y_{C02} \cdot c_{p,C02} + y_{H20} \cdot c_{p,H20}$  (28)

Where  $y_i$  terms indicate the mass fraction of each components.

Additionally, a third degree polynomial equation is implemented in order to account for the specific heat at constant pressure dependence on temperature, according to Equation (29) [44]:

$$c_{p,j}(T) = A_j + B_j \cdot T + C_j \cdot T^2 + D_j \cdot T^3$$
<sup>(29)</sup>

Thus, all of the polynomial coefficients for calculation are

Table 5 K-factors for  $H_2NG$  mixtures. (numerical values are based on  $[O_2]=4\%$  and  $T_{av}=$  50  $^\circ C).$ 

<i>f</i> <sub>H2</sub> [% vol.]	<i>K</i> <sub>1</sub>	<i>K</i> <sub>2</sub>	<i>K</i> <sub>3</sub>
0%	0.007852	2.27425E-05	0.004384
5%	0.007831	2.25689E-05	0.004322
10%	0.007808	2.23817E-05	0.004255
15%	0.007783	2.21794E-05	0.004183
20%	0.007756	2.19601E-05	0.004104
25%	0.007727	2.17215E-05	0.004019
30%	0.007695	2.14608E-05	0.003925

620

1.20

1.18

reported in Table 6.

Combining those equations, the H<sub>2</sub>NG by-products specific heats at constant pressure, as the oxygen concentration function, are plotted in Fig. 4, with changes in hydrogen content. In detail, the oxygen amount within the exhaust gases ranges between 0% vol. and 15% vol. (i.e.  $1 \leq \lambda \leq 3.542$ ).

Even though the mixtures Lower Flammability Limits (LFL) are below the maximum value of 2.878 corresponding to  $[O_2]$  and %H<sub>2</sub> equal to 13.63% vol. and 30% vol., respectively. Those limits are computed by the following empiric formula provided by Miao H. et al. [45]:

$$LFL = \left(2.5 \cdot f_{H2}^2 - 2.5 \cdot f_{H2} + 5\right) \cdot 100 \tag{30}$$

Thereafter, the relative equivalence ratios corresponding to the lower flammability limits are computed accounting for the results deriving from Equation (30) and are shown in Table 7.

Looking at Fig. 4, it is possible to state that the exhaust gas specific heat values are slightly affected by the burner combustion set-up. Indeed, as the oxygen concentration increases from 0% vol. up to 15% vol. the specific heat values drop down for each mixture (see Table 8), entailing a maximum reduction equal to 9.825%, for H<sub>2</sub>NG@30%, compared to the stoichiometric conditions. As a consequence, in order to investigate on the calculation error extent, owing to the previous assumption for the reference relative equivalence ratio, the error analysis on exhaust gas  $c_p$  calculation is carried out by shortening the oxygen range from 0% to 15% vol. to 0%-7% vol. with changes in oxygen concentration ranging in that limited span. In that case, an oxygen concentration equal to 7% corresponds to the  $\lambda$  value of 1.501, which is a typical limit threshold for methane lean combustion in boiler burners. Therefore, under that hypothesis the maximum reduction of specific heat values is limited to 3.5% approximately, as reported in Table 8.

The same approach is used to analyse the effect of reference temperature variations on specific heats calculation. Having fixed the oxygen concentration equal to 4% vol., the specific heat values of the exhaust gases are calculated with varying the reference average temperature in the range of 40 °C–61 °C. In Fig. 5, the error analysis results are depicted so as to evaluate rapidly the overestimation and underestimation owing to the use of those reference values. It is remarkable that the specific heat is less sensitive to the temperature variations than those related to the oxygen concentration.

Finally, the overall sensitivity analysis outcomes are presented in Fig. 6 by means of six different spider graphs. They allow to evaluate by a linear combination, the cumulative error when the variables change within the span of -19% + 22%.

To recap, the use of the K-factors values reported in Table 5 leads to a sensible heat loss overestimation limited to 0.235% when the real average temperature is lower than 50 °C. While, it leads to an underestimation equal to 0.237% as the real average temperature is higher. Similarly, when the real oxygen concentration is higher than 4% vol., an overestimation equal to 1.57% occurs and, in the opposite case, an underestimation of 2% can be noticed.

Table 6Coefficients for the specific heat calculation of exhaust gas components [44].

C [kJ/kg K<sup>3</sup>]

9.571 E-07

-1.899 E-07

-1.273 E-06

5.861 E-07

D [kJ/kg K4]

4.097 E-10

3.890 E-10

-1.998 E-10

-4.171 E-10

Table 7

B [kJ/kg K<sup>2</sup>]

-0.000485

0.000362

0.001669

0.001069

A [kJ/kg K]

1.112500

0.909375

0.450000

1.791111

 $N_2$ 

02

 $CO_2$ 

H<sub>2</sub>O



f <sub>H2</sub> [%vol.]	0%	5%	10%	15%	20%	25%	30%
λ <sub>limit</sub>	1.986	2.116	2.253	2.398	2.550	2.710	2.878



**Fig. 4.** Specific heat at constant pressure of exhaust gas vs. oxygen concentration with varying hydrogen fraction.

#### 4.2. H<sub>2</sub>NG effects on condensing boilers

In this section the  $H_2NG$  blends condensing properties, such as the theoretical condensable water, the water molar fraction within exhaust gases and dew point temperatures are presented along with the implications of the hydrogen contribution to the Lower and Higher Heating Values of the mixtures.

Referring to Equation (18), it is possible to calculate easily the water content in exhaust gases and its molar fraction which is strictly correlated to the dew point temperature. Additionally, when a lean combustion is set, the volumetric water concentration decreases as the relative equivalence ratio rises owing to the air dilution effect.

Looking at Table 9, it emerges that by adding more hydrogen to methane and burning the mixture in stoichiometric conditions, the water saturation temperature increases slightly whilst the available energy per unit volume of fuel tends to lessen as well as the latent heat.

In order to evaluate how this latter contributes to the maximum available energy for each mixture, in condensing applications, the HVR (heating value ratio) is identified as the useful parameter. It is the ratio between the HHV (higher heating value) and the LHV (lower heating value) of the blends. It can be noticed that the larger is the numerical value, the larger will be the maximum recoverable heat by condensation as depicted in Fig. 7.

Moreover, when the whole water content is condensed out, the maximum available energy does not increase linearly with increasing hydrogen volumetric percentage.

Given that the  $H_2NG$  blends volumetric heating values are lower than the methane one, a higher blend flow rate is required to provide the same thermal energy output related to 1 Nm<sup>3</sup>/h of NG. For instance, when  $H_2NG@$  15%vol.is burnt the required flow rate is

0%

5%

10%

-15%

#### Table 8

Specific heat at constant pressure variations compared with the stoichiometric combustion conditions.

<i>f</i> <sub>H2</sub> [%]vol.	0%	5%	10%	15%	20%	25%	30%
Max Percentage reductions	-8.775%	-8.918%	-9.071%	-9.237%	-9.417%	-9.612%	-9.825%
Max Percentage reductions for boiler range	-3.146%	-3.196%	-3.248%	-3.306%	-3.367%	-3.434%	-3.507%



Fig. 5. Reference temperature variation effects on specific heat at constant pressure calculation vs. hydrogen fraction (blue bars represent the absolute errors). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

equal to 1.117  $\text{Nm}^3/\text{h}$ . As a consequence, despite of the specific water content per H<sub>2</sub>NG cubic meter being lower than the NG one, the total condensable water mass is higher (e.g. 1.6595 kg <sub>H2O</sub>/h for H<sub>2</sub>NG@ 15%vol.).

In order to calculate the EFC value, previously mentioned in Equation (14), a simplified procedure is adopted instead of complex heat and mass transfer calculation models. To do so, it is possible to correlate the specific water content by volume of dry exhaust gases with their output temperature.

The specific water content by volume of dry exhaust gas reads as:

$$\delta = \frac{m_{H2O}}{V_{exh,dry}} \left[ \frac{g}{Nm^3} \right]$$
(31)

Consequently, the water molar fraction can be expressed by:

$$x_{H2O} = \delta \cdot \frac{V_{exh,dry}}{\rho_{n,H2O} \cdot V_{exh,wet}} = \delta \cdot \frac{R_v}{\rho_{H2O}}$$
(32)

Where  $R_{\nu} = \frac{V_{exh,dy}}{V_{exh,wet}}$  represents the dry volume to wet volume exhaust ratio. This latter results strongly dependent on both hydrogen fraction and oxygen concentration, as shown in Table 10 in a systemic overview. It decreases as the hydrogen fraction increases, and it enhances as the combustion is leaner.

From Equation (32), it results that the specific water content by volume  $\delta$  is a temperature function (Equation (33)), having considered the Dalton's Law and equated saturation pressure to the water partial pressure within exhaust gas, as in Equation (34).

$$\delta = f(T) \tag{33}$$

$$p_{sat}(T) = p_{ref} \cdot x_{H2O} \tag{34}$$

Specifically, the analytical formulation of Equation (33)derives from rearranging the saturation-pressure equation developed by IAPWS-IF97 [46] explained in detail in Ref. [47]. It is remarkable that in Ref. [47] this procedure was already validated by the authors during an experimental campaign which was carried out on a condensing  $\mu$ CHP designed for dwelling applications.

Having said, each mixture is characterised by a maximum  $\delta$  value which corresponds to its dew point temperature. This latter  $\delta_{max}$ , together with the measured  $\delta$  to the boiler stack, allows to evaluate the actual Condensed out Water Mass (CWM) by their difference:

$$CWM = (\delta_{\max} - \delta) \left[ \frac{g_{H2O}}{Nm_{exh,dry}^3} \right]$$
(35)

Then, by Equation (35) it is possible to calculate the condensation efficiency  $\eta_{cond}$ , defined in Ref. [48] as the ratio between the actual condensed out water mass and the maximum condensable one.

$$\eta_{cond} = \frac{\delta_{max} - \delta}{\delta_{max}} \tag{36}$$

That parameter can be also deduced graphically by the use of maps reported in Figs. 8 and 9. With this methodology, the



**Fig. 6.** Spider graphs for sensitivity analysis when temperature and relative equivalence ratio have the same normalised variation. Part a) it refers to H<sub>2</sub>NG@5%; Part b) it refers to H<sub>2</sub>NG@10%; Part c) it refers to H<sub>2</sub>NG@15%; Part d) it refers to H<sub>2</sub>NG@20%; Part e) it refers to H<sub>2</sub>NG@25%; Part f) it refers to H<sub>2</sub>NG@30%.

#### Table 9

 $H_2NG$  condensation properties with changes in the %  $H_2$  vol.

f <sub>H2</sub> [%]vol.	Water partial pressure [bar]	x <sub>H2O</sub> [%]vol.	T <sub>sat</sub> [°C]	l <sub>H</sub> [kJ/kg <sub>H2O</sub> ]	Available energy [kWh/Nm <sup>3</sup> fuel]
0%	0.1917	18.9229%	59.14	2359.781	1.0528
15%	0.1990	19.6439%	59.95	2357.814	0.9730
30%	0.2083	20.5659%	60.94	2355.384	0.8932



Fig. 7. Heating Values Ratio and maximum water content per unit volume of fuel vs. hydrogen volumetric fraction.

#### Table 10

-Dry volume to wet volume exhaust ratio values with changes in oxygen concentration and hydrogen fraction in the blend.

$R_{\nu} = R(\lambda)_{\nu} [ Nm_{exh,dry}^3/Nm_{exh,wet}^3]$									
%O <sub>2</sub>	λ	f <sub>H2</sub> [% vo	ol.]						
		0%	5%	10%	15%	20%	25%	30%	
0%	1.000	0.8108	0.8086	0.8062	0.8036	0.8008	0.7977	0.7943	
7%	1.504	0.8656	0.8639	0.8621	0.8602	0.8580	0.8557	0.8531	
18%	7.207	0.9686	0.9682	0.9677	0.9672	0.9666	0.9660	0.9653	

information about heat exchanger geometry and its surfaces extension can be neglected, for identifying the latent heat contribution on the recoverable energy.

Therefore, the only input value is the exhaust gas temperature to the stack, measured by a dedicated probe to determine the specific water content. Then, taking into account the hydrogen volumetric fraction, the condensation efficiency is estimated.

Finally, considering the HVR values reported in Fig. 7, the Energy Fraction of Condensation (EFC) defined in Equation (14) reads as:





Fig. 9. Map for condensation efficiency assessment related to H<sub>2</sub>NG blends with changes in % H2 vol. (temperature range 49 °C - 35 °C).

$$EFC = (HVR - 1) \cdot \eta_{cond} \tag{37}$$

### 4.2.1. Relative equivalence ratio influence on dew point

temperature and on condensation efficiency

It is well known that a lean combustion set-up for burners

entails an oxygen concentration in exhaust gases higher than zero compared with stoichiometric conditions, and the nitrogen fraction increases as well. The presence of those chemical species results in a higher exhaust gases volume, diluting the water vapour molar fraction. Consequently, the water partial pressure as well as the dew point temperature values decline penalizing the heat recovery effectiveness related to condensing applications.

In Fig. 10, four maps related to the saturation temperature trend,



Fig. 10. Dew point temperatures vs. oxygen concentration in exhaust gas with changes in hydrogen fraction.

caused by the growing oxygen concentration, are reported. Since the saturation temperature rises as the hydrogen fraction increases, the H<sub>2</sub>NG blends are able to burn leaner than NG due to also their faster laminar speed burning, improving the mixtures combustion stability [49,50]. Consequently, the same by-products dew point temperature are achievable with different burner set-up.

For instance, the NG combustion characterized by a relative equivalence ratio equal to 1.26 is equivalent to the  $H_2NG@30\%$  burning with a relative equivalence ratio equal to 1.4. It entails that

the water dew point temperature in the exhaust gases corresponds to 55 °C for both gaseous fuels. Thus, it is important to point out that the H<sub>2</sub>NG lean combustion leads to a NO<sub>x</sub> emissions reduction owing to a lower flame temperature within the combustion chamber, mitigating the hydrogen contribution to nitrous compounds formation.

 Table 11

 Maximum specific water content by volume of dry exhaust gas as the oxygen concentration function, with varying the hydrogen fraction in the blend.

$\delta_{\text{max}}$	[g <sub>H2O</sub> /Nn	n <sup>3</sup> exh]						
%02	λ	$f_{H2}$						
		0%	5%	10%	15%	20%	25%	30%
0%	1.000	187.43	190.15	193.10	196.32	199.82	203.67	207.91
1%	1.050	178.46	181.05	183.86	186.92	190.26	193.93	197.97
2%	1.106	169.49	171.95	174.62	177.53	180.70	184.18	188.02
3%	1.168	160.52	162.86	165.38	168.14	171.14	174.44	178.07
4%	1.237	151.56	153.76	156.14	158.74	161.58	164.69	168.12
5%	1.314	142.59	144.66	146.91	149.35	152.02	154.95	158.17
6%	1.403	133.62	135.56	137.67	139.96	142.46	145.20	148.23
7%	1.504	124.65	126.46	128.43	130.56	132.90	135.46	138.28
8%	1.620	115.69	117.37	119.19	121.17	123.34	125.71	128.33
9%	1.756	106.72	108.27	109.95	111.78	113.78	115.97	118.38
10%	1.917	97.75	99.17	100.71	102.38	104.21	106.22	108.43
11%	2.111	88.78	90.07	91.47	92.99	94.65	96.48	98.49
12%	2.348	79.81	80.97	82.23	83.60	85.09	86.73	88.54
13%	2.646	70.85	71.87	72.99	74.21	75.53	76.99	78.59
14%	3.029	61.88	62.78	63.75	64.81	65.97	67.24	68.64
15%	3.542	52.91	53.68	54.51	55.42	56.41	57.50	58.69
16%	4.265	43.94	44.58	45.27	46.03	46.85	47.75	48.75
17%	5.359	34.97	35.48	36.03	36.63	37.29	38.01	38.80
18%	7.207	26.01	26.38	26.79	27.24	27.73	28.26	28.85

Therefore, a compromise between energy and environmental issues has to be reached in order to fully exploit the  $H_2NG$  properties in condensing boilers.

Thereafter, since the dew point temperature declines, the maximum specific water content by volume of dry exhaust gases is influenced similarly. In Table 11, the reference values for  $\delta_{max}$  as the oxygen concentration function, with changes in hydrogen enrichment, are outlined. Those parameters are strictly related to the condensation efficiency calculation, reducing its value as the fuel combustion is leaner.

Consequently, whether the same discharging temperature of by-products was registered by the gas analyser probe, the condensation efficiency will be largely lower compared to the stoichiometric combustion conditions. It is noteworthy that the water molar fraction is univocally determined by saturation temperature and fuel typology, so the mass water content results constant in both stoichiometric and lean combustion under the same thermodynamic conditions. For these reasons, when an air excess is set-up, Equation (31) denominator tends to increase hyperbolically, according to Equation (A.17). The condensation efficiency calculated in stoichiometric conditions can be corrected by a multiplier factor defined in Equation (38):

$$K_{\eta} = \frac{\eta(\lambda)_{cond}}{\eta_{cond}} = \left(\frac{\delta(\lambda)_{max} - \frac{x_{H20} \cdot \rho_{n,H20}}{K_{RV} \cdot R_{\nu}}}{\delta_{max} - \frac{x_{H20} \cdot \rho_{n,H20}}{R_{\nu}}}\right) \cdot \lambda$$
(38)

Where K<sub>RV</sub>reads as:

$$K_{RV} = \frac{R(\lambda)_{\nu}}{R_{\nu}} \tag{39}$$

Here,  $R(\lambda)_{\nu}$  denotes the dry volume to wet volume ratio of exhaust depending on air excess while,  $R_{\nu}$  refers to the same parameter calculated referring to the stoichiometric combustion. Finally, in order to simplify that correction procedure six different  $K_{\eta}$ -charts are built for each H<sub>2</sub>NG mixture as depicted in Figs. 11–16.

#### 4.2.2. Effects of air water content

The outdoor environmental conditions changes during machines operation are usually the main factors which lead to the offdesign and derating of energy conversion systems. In detail, the air temperature, along with the relative humidity, influence differently the air density and the water mass amount which take part in



Fig. 11. Correction factor chart for condensation efficiency in lean combustion. Reference mixture: H<sub>2</sub>NG @5%;  $K_{\eta}$  values vs. specific water content with changes in oxygen concentration.



Fig. 12. Correction factor chart for condensation efficiency in lean combustion. Reference mixture: H<sub>2</sub>NG @10%; K<sub>η</sub> values vs. specific water content with changes in oxygen concentration.

combustion processes energy balance. Once the water fraction increases, the flame temperature tends to drop down due to the latent heat negative contribution, subtracting energy from fuels combustion in favour of water phase change.

Nevertheless, a small flame temperature reduction in boiler

burners, caused by the moisture presence, on one hand, implies environmental benefits in terms of thermal  $NO_x$  mitigation; on the other hand, CO emissions can rise owing to a higher incomplete combustion degree, but energy gains are achievable anyhow.

Indeed, the larger the specific water content in exhaust for



Fig. 13. Correction factor chart for condensation efficiency in lean combustion. Reference mixture: H<sub>2</sub>NG @15%;  $K_{\eta}$  values vs. specific water content with changes in oxygen concentration.



Fig. 14. Correction factor chart for condensation efficiency in lean combustion. Reference mixture: H<sub>2</sub>NG @20%;  $K_{\eta}$  values vs. specific water content with changes in oxygen concentration.

condensing out, the larger the recoverable heat fraction is, at the same cooling temperature. Fig. 17 depicts schematically the overall water mass balance and the energy gain evaluation according to the

current measurement procedure which UNI 10389 calls for. In order to estimate properly the H<sub>2</sub>NG mixtures advantages in condensing boilers, accounting for the moisture doping effect on



Fig. 15. Correction factor chart for condensation efficiency in lean combustion. Reference mixture: H<sub>2</sub>NG @25%; K<sub>η</sub> values vs. specific water content with changes in oxygen concentration.



Fig. 16. Correction factor chart for condensation efficiency in lean combustion. Reference mixture: H<sub>2</sub>NG @30%;  $K_{\eta}$  values vs. specific water content with changes in oxygen concentration.

measurement is crucial.

From the water mass balance reported in Equation (40), it is possible to define a new theoretical specific water content  $\delta'_{max}$  by dividing those quantities by the exhaust volume dry, as shown in Equation (41):

$$m_{\rm H2O,tot} = m_{\rm H2O,air} + m_{\rm H2O,exh} \tag{40}$$

$$\delta'_{max} = \delta_{max} + \delta_{air} \tag{41}$$

Where:



$$m_{H20,air} = m_{air} \cdot X_{H20,air} \tag{43}$$

The parameter defined in Equation (42) represents the air contribution to the water mass content in exhaust and  $X_{H2O,air}$  in Equation (43) indicates the absolute humidity which can be deduced by a traditional psychrometric chart.

Consequently, it is possible to correct easily the  $\delta_{max}$  values provided in Table 11, by the following multiplier:



Fig. 17. Simplified scheme of measurement procedure for condensing boiler efficiency assessment.

Table 12				
Absolute humidity	values with changes	in outdoor tem	perature and	relative humidity

T [°C]	Relative Humidity										
	40.0%	45.0%	50.0%	55.0%	60.0%	65.0%	70.0%	75.0%	80.0%	85.0%	90.0%
-20	0.2547	0.2866	0.3184	0.3503	0.3822	0.414	0.4459	0.4778	0.5097	0.5415	0.5734
-18	0.3081	0.3467	0.3852	0.4238	0.4624	0.5009	0.5395	0.5781	0.6167	0.6552	0.6938
-16	0.3717	0.4182	0.4647	0.5112	0.5578	0.6043	0.6508	0.6974	0.7439	0.7905	0.837
-14	0.4471	0.503	0.559	0.6149	0.6709	0.7269	0.7829	0.8389	0.8949	0.9509	1.006
-12	0.5362	0.6033	0.6705	0.7376	0.8047	0.8719	0.9391	1.006	1.073	1.14	1.207
-10	0.6414	0.7217	0.802	0.8823	0.9626	1.043	1.123	1.203	1.284	1.364	1.445
-8	0.7651	0.8609	0.9567	1.052	1.148	1.244	1.34	1.436	1.532	1.628	1.724
-6	0.9103	1.024	1.138	1.252	1.366	1.48	1.594	1.709	1.823	1.937	2.052
-4	1.08	1.215	1.351	1.486	1.621	1.757	1.893	2.028	2.164	2.3	2.436
-2	1.278	1.439	1.599	1.759	1.92	2.08	2.241	2.402	2.563	2.724	2.884
0	1.51	1.699	1.888	2.078	2.267	2.457	2.647	2.837	3.027	3.217	3.407
2	1.744	1.963	2.182	2.401	2.621	2.84	3.06	3.279	3.499	3.719	3.939
4	2.011	2.263	2.516	2.769	3.022	3.275	3.528	3.782	4.036	4.29	4.544
6	2.313	2.604	2.894	3.185	3.477	3.768	4.06	4.352	4.644	4.937	5.23
8	2.655	2.989	3.323	3.657	3.991	4.326	4.662	4.997	5.333	5.67	6.007
10	3.041	3.423	3.806	4.189	4.573	4.957	5.342	5.727	6.112	6.499	6.885



Fig. 18. Water mass content in air per unit of fuel in stoichiometric combustion vs. outdoor temperature. Part a) pure NG combustion with changes in air relative humidity; Part b) reference relative humidity equal to 40% with change in hydrogen fraction; Part c) reference relative humidity equal to 50% with change in hydrogen fraction; Part d) reference relative humidity equal to 90% with change in hydrogen fraction.

		$\frac{RH=50\%}{M_{w,air50}}$	$\frac{\text{RH}=40\%}{M_{\text{w,air40}}}$	$\frac{RH=90\%}{M_{w,air90}}$	$\frac{e_{min}}{\frac{M_{w,air40}-M_{w,air50}}{M_{w,air50}}}$	$\frac{e_{\max}}{\frac{M_{\text{w,air50}}-M_{\text{w,air50}}}{M_{\text{w,air50}}}}$
5% vol. H <sub>2</sub>	$T_{air} = 0 \ ^{\circ}C$	22.3716	17.8925	40.3707	-20.02%	80.456%
	$T_{air} = 10 \ ^{\circ}C$	45.0986	36.0338	81.5827	-20.02%	80.456%
30% vol. H <sub>2</sub>	$T_{air} = 0 \ ^\circ C$	18.0133	14.4068	32.5059	-20.02%	80.456%
	$T_{air} = 10 \ ^\circ C$	36.3128	29.0140	65.6893	-20.02%	80.456%

Table 13 Total water mass content in the air for H<sub>2</sub>NG at 5% and 10% and relative errors assessment. Reference values: air temperature 0 °C and 10 °C; Relative humidity 40%, 50%, 90%.

$$K_{WA} = 1 + \frac{\delta_{air}}{\delta_{max}} \tag{44}$$

Finally, in order to facilitate the calculation related to the water mass content in the air, the absolute humidity values are outlined in Table 12 with changes in outdoor temperature and relative humidity, ranging from -20 °C to 10 °C and 40%–90%, respectively.

# 4.2.3. Error analysis on EFC calculation related to the air relative humidity changes

In order to complete the analysis of H<sub>2</sub>NG influence on energy performance assessment, the error driven by the actual value of relative humidity of the air during boilers operation, compared to the reference one, has been evaluated. The authors believe that this issue has to be discussed to avoid not realistic measurements of boilers combustion efficiency when they are fuelled with H<sub>2</sub>NG blends and the outdoor environmental conditions change. In the matter of condensing boiler thermal efficiency, the error has been described as a function of hydrogen enrichment and the actual relative humidity during the combustion. A relative humidity equal to 50% has been assumed as the reference value for error calculation, since this is the suggested one by current regulations. The lower and upper limits in actual operating conditions for relative humidity are assumed equal to 40% and 90%, respectively, in order to account for the most common variation of outdoor weather conditions.

Having said, the Energy Fraction of Condensation (EFC) can be

rearranged as follows:

$$EFC = (HVR - 1) \cdot \left(1 - \frac{\delta(T)}{\delta'_{max}}\right)$$
(45)

Thus, by applying the fundamental law of error propagation [51] and by differentiating the EFC, the following quantities have been obtained:

$$\frac{d(EFC)}{d\left(\delta'_{max}\right)} = (HVR - 1) \cdot \frac{\delta(T)}{\left(\delta'_{max}\right)^2}$$
(46)

Then, in Equation (47), the EFC relative error reads as:

$$e(EFC) = \frac{d(EFC)}{EFC} = \frac{\delta(T)}{\delta'_{max} - \delta(T)} \cdot e\left(\delta'_{max}\right)$$
(47)

Here, Equation (48) denotes the relative error associated to  $\delta'_{max}$  evaluation:

$$e\left(\delta_{max}^{'}\right) = \frac{d\left(\delta_{max}^{'}\right)}{\delta_{max}^{'}} \tag{48}$$

Given that  $\delta_{air}$  is independent of relative equivalence ratio, it is possible to state that e(EFC) is function of hydrogen content, of the air specific humidity in stoichiometric combustion conditions and of the relative error associated to  $\delta'_{max}$  evaluation. This latter does



Fig. 19. Energy Fraction of Condensation vs. %H<sub>2</sub> vol. with changes in air Relative Humidity.

not change with varying the outdoor air temperature for a fixed hydrogen fraction. Furthermore, it is noteworthy that changes in  $f_{H2}$ lead to the same e ( $\delta'_{max}$ ), too. For instance, referring to all of data depicted in Fig. 18, the maximum and minimum relative errors are calculated for two  $H_2NG$  blends, i.e. 5%vol. and 30%vol., at two air temperatures: 0 °C and 10 °C. For all the combinations, those errors are equal to 80.456% and 20.02%, respectively. Table 13 outlines all of values for calculation.

So, Equation (47) can be rearranged as:

$$e(EFC) = A(f_{H2}, \delta_{air}) \cdot e\left(\delta'_{max}\right)$$
(49)

In order to evaluate the effects on the final EFC value, calculations are performed by assuming an exhaust gas temperature measured by a probe equal to 45 °C, which corresponds to  $\delta(T) = 84.57~g_{H2O}/Nm^3_{exh,dry}$ . In Fig. 19, the EFC values vs. hydrogen fraction along with the error range are reported.

To sum up, the hydrogen enrichment leads to a maximum EFC enhancement of 0.9% points for H<sub>2</sub>NG@30% vol. While, the relative humidity plays a key role for the actual EFC value, which can rise up to 4.8% points at RH = 90% compared to the reference condition. It entails that the RH measurement during the combustion test is crucial for the correct assessment of condensing boiler thermal efficiency.

#### 5. Conclusions

The boilers combustion efficiency variations, caused by the hydrogen enrichment in NG, are investigated complying with current technical standards. Specifically, technical issues related to traditional and condensing boilers are addressed and widely discussed; highlighting the potential energy benefits related to the higher specific water content in H<sub>2</sub>NG blends by-products whether the water was condensed out. The research project outcomes can be summed up as follows:

- The analytical procedure based on chemical balance equations, for H<sub>2</sub>NG blends Ostwald charts construction, is presented.
- According to the technical procedure called for UNI 10389, related to the boiler combustion efficiency assessment, the H<sub>2</sub>-enriched gaseous fuels characteristic parameters are calculated by the energy and mass balances. From data, it emerged that *K*<sub>1</sub>, *K*<sub>2</sub> and *K*<sub>3</sub> values diminish as hydrogen volumetric fraction increases and with the same recorded exhaust gas temperature the boiler efficiency rises, accordingly. Furthermore, all the three K-coefficients depend on specific heat value of the exhaust gas, on the air excess and the reference temperature for calculating it as well.
- A sensitivity analysis on specific heat calculation is carried out. It is remarkable that the specific heat is less sensitive to the temperature variations than those related to the oxygen concentration. On the contrary, it is more affected by the burner combustion set-up. Indeed, as the oxygen concentration ranges from 0% vol. up to 15% vol. the specific heat values drop nonlinearly down for each mixture, showing a maximum reduction equal to 9.825%, for H<sub>2</sub>NG@30%, compared to the stoichiometric conditions. As a consequence, the use of the K-factors calculated in Table 5 leads to a sensible heat loss overestimation limited to 0.235% when the real average temperature is lower than 50 °C. While, it leads to an underestimation equal to 0.237% as the real average temperature is higher. Similarly, when the actual oxygen concentration is higher than 4% vol., an overestimation equal to 1.57% occurs and, in the opposite case, an underestimation of 2% can be noticed.

- H<sub>2</sub>NG mixtures condensation properties are presented. So, adding more hydrogen to methane and burning the mixture in stoichiometric conditions, the dew point temperature increases slightly whilst the available energy per unit volume of fuel tends to lessen as well as the latent heat. Thus, the air excess reduces largely the dew point temperature penalising the condensation efficiency. In order to take into account this drawback correction factor charts are developed.
- Finally, a maximum EFC enhancement of 0.9% points is noticed for  $H_2NG@30\%$  vol. While, the relative humidity plays a key role for the actual EFC value. It can rise up to 4.8% points at RH = 90% compared to the reference condition. For that reason, the RH measurement during the combustion test is crucial for condensing boiler combustion efficiency.

In the end, with this work the authors set the ground for using an upgraded procedure in the forthcoming experimental campaign dealing with the environmental and energy characterization of a condensing boiler fuelled with H<sub>2</sub>NG blends.

#### Nomenclature

[CO] <sub>act</sub>	Measured carbon oxide concentration [% vol.]
[CO] <sub>th</sub>	Theoretical carbon monoxide concentration [% vol.]
[CO] <sub>vol</sub>	Carbon monoxide concentration [% vol.]
$[CO_2]_{act}$	Measured carbon dioxide concentration [% vol.]
$[CO_2]_{th}$	Theoretical carbon dioxide concentration [% vol.]
[O <sub>2</sub> ]	Measured oxygen concentration
A <sub>i</sub>	j-th coefficient A for the specific heat calculation of
5	exhaust gas component
Bi	j-th coefficient B for the specific heat calculation of
5	exhaust gas component
С	Carbon mass fraction within the fuel [kg/kg <sub>fuel</sub> ]
CH <sub>4</sub>	Methane
Ci	j-th coefficient C for the specific heat calculation of
5	exhaust gas component
CO	Carbon Monoxide
CO <sub>2</sub>	Carbon Dioxide
c <sub>p,CO2</sub>	Carbon dioxide specific heat at constant pressure [k]/kg K
c <sub>p,exh</sub>	Exhaust gas average specific heat at constant pressure [k]
-	kg K]
c <sub>p,H2O</sub>	Water vapour specific heat at constant pressure [kJ/kg K
c <sub>p,j</sub>	Generic element Specific heat at constant pressure[kJ/kg
	K]
c <sub>p,N2</sub>	Nitrogen specific heat at constant pressure [kJ/kg K]
c <sub>p,O2</sub>	Oxygen specific heat at constant pressure [kJ/kg K]
Dj	j-th coefficient D for the specific heat calculation of
	exhaust gas component
E	Percentage air excess [%]
$e_{\rm max}$	Maximum relative error [%]
e <sub>min</sub>	Minimum relative error [%]
f <sub>H2</sub>	Volumetric Hydrogen fraction in the blend [%vol.]
h	Hydrogen mass fraction within the fuel [kg/kg <sub>fuel</sub> ]
H <sub>2</sub>	Hydrogen
H <sub>2</sub> NG	Hydrogen enriched Natural Gas
$H_2O$	Water
K <sub>1</sub>	Coefficient 1 for sensible heat loss formula $[K^{-1}]$
K <sub>2</sub>	Coefficient 2 for sensible heat loss formula $[K^{-1}]$
K <sub>3</sub>	Coefficient 3 for sensible heat loss formula [K <sup>-1</sup> ]
K <sub>RV</sub>	Correction factor for R <sub>v</sub> ratio
K <sub>WA</sub>	Correction factor for water content in the air
Kη	Correction factor for condensation efficiency in lean
,	combustion
IH	Latent neat [kJ/kg]
m <sub>air</sub>	Dry air mass [kg]

m <sub>exh</sub>	Exhaust mass flow rate [kg/s]
m <sub>fuel</sub>	Fuel mass flow rate [kg/s]
m <sub>H20</sub>	Water mass content in exhaust [g]
m <sub>H2O,air</sub>	Water mass content in air [g]
m <sub>H2O,cond</sub>	dens Condensed out water mass [g]
m <sub>H20,exh</sub>	Water mass content in exhaust due to fuel combustion [g]
m <sub>H2O,resid</sub>	<sub>dual</sub> Residual water mass content in exhaust [g]
m <sub>H2O,tot</sub>	Total water mass content in exhaust [g]
M <sub>w,air40</sub>	Water mass content in the air per unit of fuel @ 40% of RH $\left[r_{e} - N\right]$
M	[gH20/INIII fuel]
IVI <sub>W,air50</sub>	$[g_{\rm upp}/\rm{Nm}^3_{\rm c}]$
Muusiroo	Water mass content in the air per unit of fuel @ 90% of RH
w,all90	$[g_{H2O}/Nm^3_{fuel}]$
N <sub>2</sub>	Nitrogen
NO <sub>x</sub>	Nitrogen Oxides
02	Oxygen
P <sub>fuel</sub>	Thermal Power from fuel burning [kW]
Platent	Thermal power from latent heat [kW]
Ploss, radiat	ive Radiative heat loss [kW]
Ploss,sens	Sensible heat loss [kW]
p <sub>ref</sub>	Reference pressure [1.013 bar]
p <sub>sat</sub>	Saturation pressure [bar]
Puseful	Useful thermal power [kW]
$R(\lambda)_v$	Dry volume to wet volume ratio of exhaust depending on
-	air excess
R <sub>d</sub>	Fuel relative density
R <sub>v</sub>	Dry volume to wet volume exhaust ratio in stoichiometric
T	conditions
l <sub>air</sub>	Air temperature [°C]
T <sub>av</sub>	Exhaust gas average temperature [°C]
Iburning	Flame temperature [°C]
УH20	Mass fraction of i th component [% wt ]
Уj Vuo	Mass fraction of nitrogen [% wt ]
УN2 Vop	Mass fraction of oxygen [% wt.]
У02 Т	Return temperature of end-user hydraulic loon [°C]
Tend-user	Exhaust gas temperature after water condensation [°C]
Texhout Texhoust	Exhaust gas temperature [°C]
Tfuel	Fuel temperature [°C]
Teat	Saturation temperature [°C]
Tsurface	Boiler case surface temperature [°C]
Vair	Actual air specific volume [Nm <sup>3</sup> /kg <sub>fuel</sub> ]
V <sub>air excess</sub>	Air excess specific volume [Nm <sup>3</sup> /kg <sub>fuel</sub> ]
V <sub>air,st</sub>	Stoichiometric specific air volume [Nm <sup>3</sup> /kg <sub>fuel</sub> ]
V'air,st	Stoichiometric air specific volume [Nm <sup>3</sup> /kg <sub>fuel</sub> ]
V <sub>CO</sub>	Actual carbon monoxide specific volume [Nm <sup>3</sup> /kg <sub>fuel</sub> ]
V <sub>CO2</sub>	Actual carbon dioxide specific volume [Nm <sup>3</sup> /kg <sub>fuel</sub> ]
V <sub>dry,exh</sub>	Specific dry exhaust volume [Nm <sup>3</sup> /kg <sub>fuel</sub> ]
V'dry,exh	Specific dry exhaust volume [Nm <sup>3</sup> /kg <sub>fuel</sub> ]
Vdry,exh,T0	DT Overall specific dry exhaust volume [Nm <sup>3</sup> /kg <sub>fuel</sub> ]
V <sub>fuel</sub>	Fuel flow rate [Nm <sup>3</sup> /s]
V <sub>02</sub>	Actual oxygen specific volume [Nm <sup>3</sup> /kg <sub>fuel</sub> ]
V <sub>O2,st</sub>	Stoichiometric oxygen specific volume [Nm <sup>3</sup> /kg <sub>fuel</sub> ]
V' <sub>O2,st</sub>	Stoichiometric oxygen specific volume [Nm <sup>3</sup> /kg <sub>fuel</sub> ]
V <sub>exh,wet</sub>	Wet Exhaust specific volume [Nm <sup>3</sup> /kg <sub>fuel</sub> ]
x <sub>H2O</sub>	vvater molar fraction [% vol.]
X <sub>H2O,air</sub>	ADSOIUTE NUMICITY [g <sub>H2O</sub> /Kg <sub>air</sub> ]
УСО2	wass naction of carbon dioxide [% Wt.]

Greek symbol

 $\alpha$  Air to fuel ratio by mass

 $\alpha_{st}$ Stoichiometric air to fuel ratio by mass $\alpha_{st,vol}$ Stoichiometric air to fuel ratio by volume

Specific water content by volume of dry exhaust gas [g/ δ Nm<sup>3</sup>] Specific water content by volume of dry exhaust gas at  $\delta(\lambda)_{max}$ dew point temperature as  $\lambda$  function [g<sub>H20</sub>/Nm<sup>3</sup>] Air contribution to the water mass content in exhaust  $\delta_{air}$  $[g_{H20}/Nm^{3}]$ Specific water content by volume of dry exhaust gas at  $\delta_{\max}$ dew point temperature [g<sub>H20</sub>/Nm<sup>3</sup>] Corrected theoretical specific water content[g<sub>H20</sub>/Nm<sup>3</sup>]  $\delta'_{max}$  $\Delta T$ Water temperature difference [°C]  $\eta(\lambda)_{condens}$  Condensation efficiency as relative equivalence ratio function Combustion efficiency  $\eta_c$ Condensation efficiency  $\eta_{condens}$ **Overall efficiency**  $\eta_{ov}$ Relative equivalence ratio λ Relative equivalence ratio at lower flammability limit  $\lambda_{limit}$ μCHP Micro Combined Heat and Power Stoichiometric air normal density [kg/Nm<sup>3</sup>] ρ<sub>air,st</sub> Fuel normal density [kg/Nm<sup>3</sup>] ρfuel Gaseous fuel normal density[kg/Nm<sup>3</sup>]  $\rho_n$ Water vapour normal density [kg/Nm<sup>3</sup>] ρ<sub>n,H2O</sub>

Abbreviations		
CHP	Combined Heat and Power	
CWM	Condensed out Water Mass	
EFC	Energy Fraction of Condensation	
HC	Hydrocarbons	
HHV	Higher Heating Value	
HVR	Heating Value Ratio	
IAPWS	International Association for Properties of Water and	
	Steam	
ICE	Internal Combustion Engine	
ISO	International Organization for Standardization	
LFL	Lower Flammability Limit	
LHV	Lower Heating Value	
NG	Natural Gas	
P2G	Power-to-Gas	
P2L	Power-to-Liquid	
RES	Renewable Energy Sources	
RH	Relative Humidity	
UNI	Italian National Organization of Standardization	

#### Appendix

Considering carbon and hydrogen chemical reactions separately, the complete and stoichiometric combustion equations read as follows:

$$C + O_2 = CO_2 \tag{A.1}$$

$$2H_2 + O_2 = 2H_2O \tag{A.2}$$

Given any hydrocarbon fuel and its elemental analysis results, it is possible to assess the exhaust gas volume dry and its products concentration.

Assuming that:

*c* indicates the carbon mass fraction within the fuel [kg/kg<sub>fuel</sub>]; *h* indicates the hydrogen mass fraction within the fuel [kg/kg<sub>fuel</sub>];

the equation for stoichiometric specific air volume  $[\text{Nm}^3/\text{kg}_{\text{fuel}}]$  reads:

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$$V_{air,st} = \frac{22,414}{0,209} \left(\frac{c}{12} + \frac{h}{4}\right)$$
(A.3)

Having considered the simplified air chemical composition, where volumetric nitrogen and oxygen concentrations are equal to 79.1% vol. and 20.9% vol. respectively, the following parameters were defined:

$$m = 0.209$$
; C = 22.414 c; H = 22.414 h;

Here, 22.414 mol/Nm<sup>3</sup> denotes the molar volume under normal condition (i.e. T = 0 °C; pressure = 1.013 bar).

Consequently, the stoichiometric oxygen and air volume can be calculated by Equation (A.4):

$$V_{O_{2,st}} = \frac{C}{12} + \frac{H}{4}; \quad V_{air,st} = \frac{V_{O_{2,st}}}{m};$$
 (A.4)

hence, the specific dry exhaust volume is reported in the equation below:

$$V_{dry\ exh} = \frac{C}{12} + \frac{1-m}{m} \left(\frac{C}{12} + \frac{H}{4}\right)$$
(A.5)

Having multiplied this equation by gaseous fuel normal density ( $\rho_n = MW_{fuel}/22.414$ ), the exhaust gas volume by fuel volume unit was obtained ( $Nm^3_{dry,exh}/Nm^3_{fuel}$ ).

Looking at Equation (A.5), it is possible to point out that the first term on the right side represents the carbon dioxide production, whereas the second one corresponds to the nitrogen volume, since water vapour deriving from hydrogen combustion has been neglected or condensed physically out within exhaust gas analyser devices.

Thus, the theoretical carbon dioxide concentration referred to the dry exhaust gas was reported below:

$$[CO_2]_{th} = \frac{\frac{C}{12}}{\frac{C}{12} + \frac{1-m}{m}\left(\frac{C}{12} + \frac{H}{4}\right)} = \frac{m}{1 + (1-m)3\frac{H}{C}}$$
(A.6)

From Equation (A.6), when the hydrogen to carbon ratio increases, the theoretical carbon dioxide concentration decreases.

When incomplete combustion occurs, the carbon monoxide formation instead of carbon dioxide can be registered. This is mainly due to the chemical kinetic mechanisms which participate during combustion process within confined domains.

Referring to stoichiometric combustion, the following chemical equations are considered:

$$C + O_2 = 2CO$$
 (A.7)

$$2H_2 + O_2 = 2H_2O \tag{A.8}$$

Using the same approach previously shown and identifying by superscript all of quantities related to this case, the following equations are obtained:

$$V'_{O_{2,st}} = \frac{C}{24} + \frac{H}{4}; \quad V'_{air,st} = \frac{V'_{O_{2,st}}}{m}$$
 (A.9)

$$V'_{exh,dry} = \frac{C}{12} + \frac{1-m}{m} \left(\frac{C}{24} + \frac{H}{4}\right)$$
 (A.10)

$$[CO]_{th} = \frac{\frac{C}{12}}{\frac{C}{12} + \frac{1-m}{m}\left(\frac{C}{24} + \frac{H}{4}\right)} = \frac{m}{1 + (1-m)\left(3\frac{H}{C} - \frac{1}{2}\right)}$$
(A.11)

Here,  $[CO]_{th}$  represents the theoretical carbon monoxide content. That term is also named as stoichiometric CO, as corrected CO, and as non-diluted CO as well.

When partially incomplete combustion process occurs in lean conditions, CO, CO<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub> are the main components in the exhaust gas as aforementioned. Therefore, the following balance equations to correlate the theoretical concentrations to the measured ones can be written:

$$V_{CO_2} = [CO_2]_{th} \cdot V_{exh,dry} = [CO_2]_{act} \cdot V_{exh,dry, TOT}$$
(A.12)

$$V_{CO} = [CO]_{th} \cdot V'_{exh,dry} = [CO]_{act} \cdot V_{exh,dry,TOT}$$
(A.13)

$$V_{O_2} = m \cdot V_{air \ excess} = [O_2] \cdot V_{exh,dry,\ TOT}$$
(A.14)

$$V_{exh,dry} + V'_{exh,dry} + V_{air\ excess} = V_{exh,dry,\ TOT}$$
(A.15)

where:V<sub>exh,dry</sub> and V'<sub>exh,dry</sub> indicate the theoretical exhaust gas volumes in stoichiometric conditions;V<sub>air excess</sub> represents the nitrogen and the oxygen volumes which do not take part during combustion reactions;V<sub>exh,air,TOT</sub> corresponds to the overall dry exhaust volume;V<sub>CO2</sub>, V<sub>CO</sub>, V<sub>O2</sub> are the actual volumes of the chemical species;[CO<sub>2</sub>]<sub>act</sub>, [CO]<sub>act</sub>, [O<sub>2</sub>] indicate the measured concentrations.

Rearranging Equation (A.15), it emerges that the overall exhaust volume is dependent on measured oxygen concentration to the stack.

$$V_{exh,dry} + V'_{exh,dry} + \frac{[O_2]}{m} V_{exh,dry, TOT} = V_{exh,dry, TOT}$$
(A.16)

Therefore, the expression for overall exhaust volume reads:

$$V_{exh,dry, TOT} = \frac{V_{exh,dry} + V_{exh,dry}}{\left(1 - \frac{[O_2]}{m}\right)}$$
(A.17)

The calculation procedure described above allows to build different charts for determining directly the carbon balance and the theoretical exhaust volume, with varying the air excess and the combustion completeness rate related to any fuel.

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