Air/methane mixture ignition with Multi-Walled Carbon Nanotubes (MWCNTs) and comparison with spark ignition

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Abstract — **The possibility to ignite the single wall carbon nanotubes (SWCNTs) containing impurities of iron in atmosphere once exposed to the radiation of a flash camera was observed for the first time in 2002. Afterwards, it was proposed to exploit this property in order to use nanostructured materials as ignition agents for fuel mixtures. Finally, in 2011 it was shown that SWCNTs can be effectively used as ignition source for an air/ethylene mixture filling a constant volume combustion chamber; the observed combustion presented the characteristics of a homogeneous-like combustion.**

In this paper a system for the ignition of an air/methane mixture is proposed, based on the exposition of multi wall carbon nanotubes (MWCNTs) to a low consumption flash camera. Namely, several experiments have been run in which 20 mg of MWCNTs, containing 75% in weight of ferrocene, have been added to an air/methane fuel mixture inside a constant volume combustion chamber. The mixture has been heated up to 373 K and the onset pressure was set equal to 3 bar. The experiments have been run varying the equivalence ratio in the range 1 - 2. The combustion process so realized has been compared to that obtained igniting the mixture with a traditional spark as in spark ignition engines. The comparison has been based on chamber pressure measurement as well as combustion process images, both sampled at a frequency equal to 2,5 kHz for an overall duration of 1.8 s.

Results confirm that the ignition triggered with MWCNTs leads to a homogeneous-like combustion, without observing a well-defined flame front propagation. The contrary is observed, as expected, with the spark assisted ignition. Moreover, dynamic pressure measurements show that, compared to spark assisted ignition, the MWCNTs photo-ignition determines a more rapid pressure gradient and a higher peak pressure which corresponds to a higher energy release rate.

Keywords— Nanotubes, HCCI, SWCNTs, MWCNTs, ignition, spark ignition engines

I. INTRODUCTION

The need to find new combustion techniques for internal combustion engines able to guarantee at the same time high efficiency and low pollutant emissions, especially in terms of nitric oxides (NO_x) and particulate, has led the researchers to study combustion processes alternative to traditional ones.

One example of alternative combustion process, named HCCI, consists in creating a homogeneous mixture between fuel and oxidizer, typical of spark ignition engines, ignited through compression thanks to the increase of the temperature during the compression phase, typical of compression ignition engines.

In this way the combustion involves the whole mixture trapped into the cylinder. The fuel consumption in HCCI engines as well as the regulated emissions (NO_x and particulate) are significantly reduced thanks to the lean and homogeneous mixture. The fundamental point of the correct operation of a HCCI engine is the precise control of the autoignition process [1,2].

The accurate control of the gaseous air/fuel mixture autoignition timing is indeed significantly complex. Using different control systems based on the control parameters mainly influencing the beginning of the combustion process, it is possible to operate an engine in HCCI conditions ideally in all the possible operating conditions; however, nowadays this result can be reached only with control strategies extremely complex and onerous [16].

In order to solve this problem, an innovative approach has been propose in order to trigger the combustion process, resulting in an intelligent synergy between optics and nanomaterials [3,4].

This system is based on the observation that carbon nanotubes, exposed to a low consumption light source, autoignite and burn. Therefore, they can eventually work as autoignition nuclei for a fuel/oxidizer mixture in contact with them. The autoignition properties of single wall carbon nanotubes (SWCNTs) exposed to the flash of a camera have been shown for the first time by Ajayan et al. in [5]. The utilization of nanostructured materials as ignition source for the fuels has been proposed and patented by Chehroudi [6,7]. In 8,9,10,11,12,13 carbon nanotubes have been used as ignition agents of a wide range of fuels, trying to generate a distributed-like combustion. Chehroudi has also proposed the application of this technique to HCCI engines, since, besides the possibility to optimize the combustion and consequently reduce the fuel consumption and the production of pollutant emissions through the control of mixture autoignition timing, allows the selection of the physical region in which to best induce the combustion. In [14] Berkowitz e Oehlschlaeger have shown that SWCNTs (containing impurities of iron by 70% in weight) introduced and mixed in a mixture of air and ethylene inside a combustion chamber and exposed to the flash of a camera, trigger the mixture combustion. The experiment has been conducted in a static combustion chamber cylindrically shaped (50,8 mm inner diameter, 76,2 mm length) made in steel, equipped with separate accesses for the flash of a camera, a piezoelectric pressure transducer, an injector of air and SWCNTs and a duct for both exhaust and ethylene introduction. An optical access is also present, allowing to acquire the camera combustion images. The experiments have highlighted that a combustion process almost homogeneous and the complete combustion of the air/ethylene mixture without an appreciable flame front propagation is obtained. The same tests have been run substituting the camera flash with a spark plug used in spark ignition engines; in this way the combustion showed a single point of ignition and the propagation of a flame front inside the combustion chamber, differently than what observed with carbon nanotubes.

In this paper, an ignition system is proposed for an air/methane mixture, based on the exposition of multi wall carbon nanotubes (MWCNTs) to the flash of a camera. Differently than SWCNTs, made by a single graphite sheet winded itself round, MWCNTs are made by more sheets coaxially wrap the one on the other. The various methodologies used for the synthesis of SWCNTs and MWCNTs, such as the chemical decomposition of steam, the laser ablation and the corona discharge, require the utilization of nanometric metal catalyzers. Ajayan et al. in [5] have verified that, while SWCNTs samples exhibited the autoignition process once exposed to the flash of a camera, MWCNTs samples do no exhibit this feature. The autoignition process with MWCNTs happens, on the contrary, if mixed with metals like palladium, iron, nickel, cobalt, aluminum, copper, zinc, potassium, sodium and titanium, [15].

In the system proposed here, MWCNTs containing the 75% weight of ferrocene have been used since their cost is notably lower compared to SWCNTs. The autoignition agents have been added to an air/methane mixture afterwards exposed to a flash light pulse. The combustion process so realized has been compared with the one obtained with a traditional spark plug used in the spark ignition engines. The idea of proposing such a combustion technique, possibly applicable in the future in a real research engine, has led to the choice of air/methane mixtures; methane, in fact, plays a role nowadays very significant for the automotive propulsion, thanks to both lower costs compared to gasoline, diesel fuel and LPG, and to the availability of bigger fuel stock compared to petrol.

II. EXPERIMENTAL LAYOUT

The experiments have been run inside a constant volume combustion chamber, aiming at comparing the combustion process characteristics of an air/methane mixture enriched with MWCNTs and ferrocene samples, with the one obtained with the traditional system used in common spark ignition engines (spark plug). During the tests, 20 mg samples of MWCNTs and ferrocene with 1:3 ration have been used. A scheme of the experimental apparatus is reported in "Fig. 1". The combustion chamber used during experiments, in low carbon steel, has a cylindrical shape with inner diameter equal to 53 mm and length equal to 270 mm. The chamber is equipped with separate accesses for a piezoresistive pressure sensor (KELLER type PA-21Y/200 bar/ 81684.33/range 0-200 bar), an exhaust line and a duct for the air/methane mixture supply, once enriched with the ignition agents. The system is also equipped with an solenoid valve (MED type BM12) required to manage the mixture amount introduced in the chamber in order to reach the desired pressure at the experiment onset (3 bar). In order to run one experiment, O_2 (20%vol.) e N_2 (80%vol.) are separately introduced inside a mixture chamber; through another duct, methane is then supplied in the same mixture chamber. The amounts of the three gaseous species is such that: 1) a final pressure of 6 bar into the mixture chamber is guaranteed; 2) the ratio between O_2 and N_2 is 1:4 and 3) the ratio between O_2, N_2 and CH_4 is such that the desired air/methane ratio is realized. The mixture so obtained is therefore heated up to 373 K thanks to a Joule effect heater, and, through the solenoid valve, introduced in the MWCNTs holder and finally into the combustion chamber. Along the chamber side, a longitudinal quartz rectangular optical access has been mounted (172 mm length x 37 mm height x 20 mm thickness). The flash (SIGMA mod EF-610DGST) has been placed into the combustion chamber. An automotive spark plug (NGK mod 4983 DCPR7E-N-10), mounted aside the chamber and supplied with a transformer (see "Fig. 1"), has been used to run the experiments and compare the combustion process obtained with MWCNTs with the process characterizing a spark ignition engine. Pressure signals have been sampled with a frequency equal to 2.5 kHz using an NI USB 6259 acquisition board, and processed through the LabVIEW NI software. By means of a CCD Memrecam GX-1F High Speed positioned in front of the quartz optical access, the images of the combustion process have been acquired with a frame rate equal to 2.5 kHz for an overall recording time equal to 1.8 s.

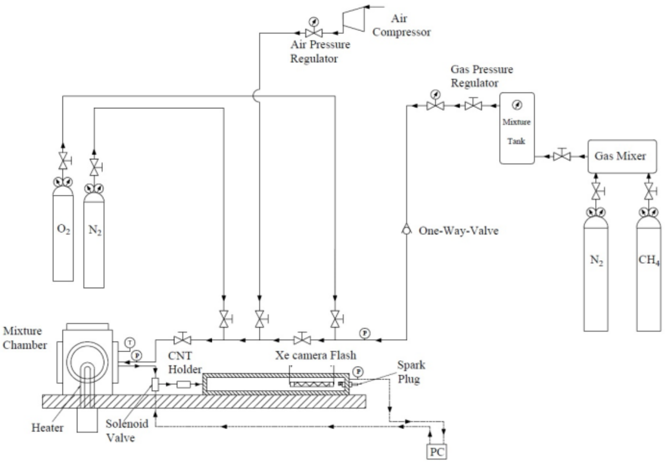

Fig. 1: Scheme of the experimental apparatus used during tests

III. RESULTS AND DISCUSSION

A. Combustion Analysis

In the following, results of the tests are reported, based on the combustion chamber pressure time history. Data obtained igniting the fuel mixture with MWCNTs and with spark plug are compared, varying the value of λ, defined as:

$$\lambda = \frac{\left(A/F\right)_{act}}{\left(A/F\right)_{st}} \tag{1}$$

where $(A/F)_{act}$ is the ratio between air and methane mass actually realized in the combustion chamber, while $(A/F)_{st}$ is the stoichiometric ratio between air and methane. Based on this definition, $\lambda=1$ denotes an actual stoichiometric mixture, while $\lambda>1$ denotes a mixture as leaner as λ exceeds 1. In this work, $(A/F)_{st}$ has been fixed equal to 17.4.

In “Fig. 2” pressure traces for MWCNTs assisted ignition, while in “Fig. 3” for spark assisted ignition are reported for different values of λ. The traces differ until t=0.2 s due to a different filling process of the combustion chamber; however it can be verified that the combustion process starts at 3 bar for both ignition methodologies. After the ignition, both curves show a rising phase due to the heat released by the fuel during combustion; the pressure reaches the peak value when all the fuel mixture has burned. Afterward, the pressure slowly decreases due to either cooling of the exhaust gases, because of the heat exchange with the chamber walls, and opening of the release valves. Therefore, the portion of the curve useful for the combustion analysis is that included from 3 bar (t=0.2 s) up to the pressure peak.

The comparison between “Fig. 2” and “Fig. 3” reveals that the combustion process triggered by MWCNTs evolves more rapidly than by spark plug. Moreover, the peak values reached in the first case are sensibly higher than in the second. Increasing λ, i.e. realizing a leaner mixture, the pressure peak delays and decreases.

In “Fig. 4” pressure peak values for MWCNTs and spark ignition are compared varying λ. It is evident that MWCNTs photo-ignition leads to a higher value of pressure peak.

It can be argued that the lower rising time and the higher pressure peak value are determined by the fact that, igniting the mixture through MWCNTs flash exposition, leads to more ignition nuclei burning more “simultaneously” and so speeding up and powering the combustion process. With the spark plug, as well know, combustion is triggered in only one point, and then proceeds thanks to the propagation of a flame front. The fuel mixture, therefore, is far from burning simultaneously.

This behavior has been confirmed thanks to direct observation of the combustion process. In “Figure 5” several pictures are reported showing how the combustion process appears after different time intervals. Pictures referring to MWCNTs photo-ignition show that the combustion involves almost all the fuel mixture filling the combustion chamber after 20 ms; the light radiation of the flame is visible basically unchanged after 60 ms.

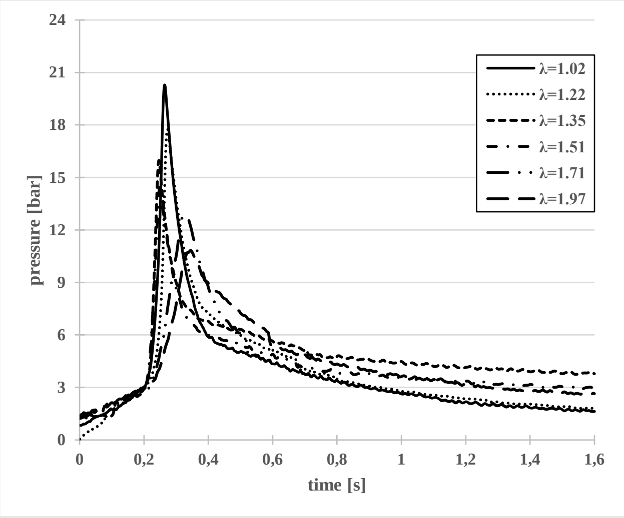

Fig. 2: Combustion pressure for the MWCNTs photo-ignition at λ ranging from 1 to 2 at initial pressure of 3 bar

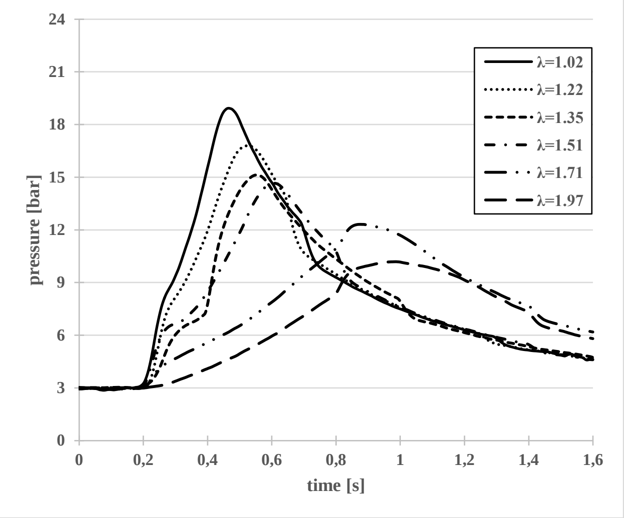

Fig. 3: Combustion pressure for the spark assisted ignition at λ ranging from 1 to 2 at initial pressure of 3 bar

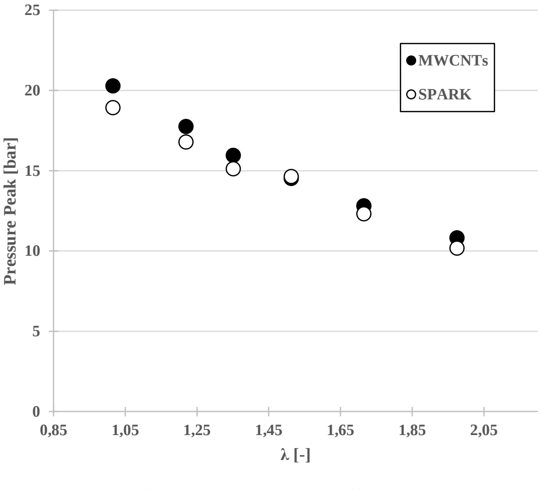

Fig. 4: Pressure peak with MWCNTs assisted and spark assisted ignition at λ ranging from 1 to 2

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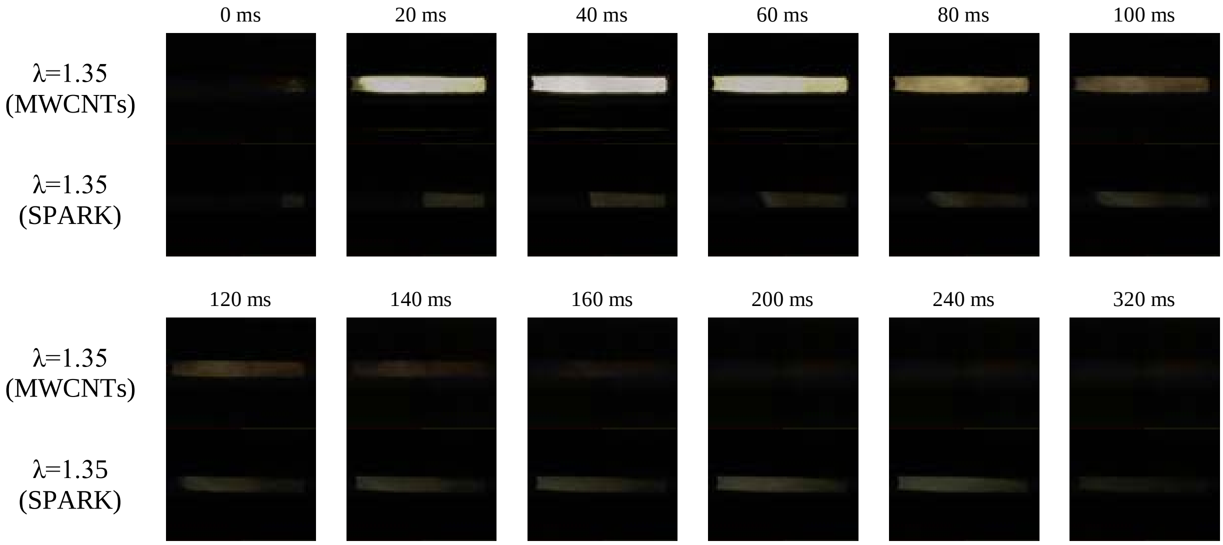

Figure 5 – Pictures of the combustion process taken at different time intervals from the combustion beginning; comparison between MWCNTs assisted and spark assisted ignition (λ=1.35)

Afterward, the radiation becomes weaker and almost null after 160 ms. The process obtained triggering the flame by means of the spark plug is substantially different: a flame front is clearly visible, traveling along the longitudinal direction of the chamber and reaching the side opposite to the spark plug only after 140 ms.

Based on the combustion pressure curves measured during the experiments, further analysis of the combustion process have been done. In particular, for a constant volume chamber and under the hypotheses of homogeneous system and negligible wall heat transfer, the Ist Law of Thermodynamics allows to estimate the rate of heat release:

$$\frac{dQ}{dt}=\frac{1}{\gamma-1}V\frac{dp}{dt} \tag{2}$$

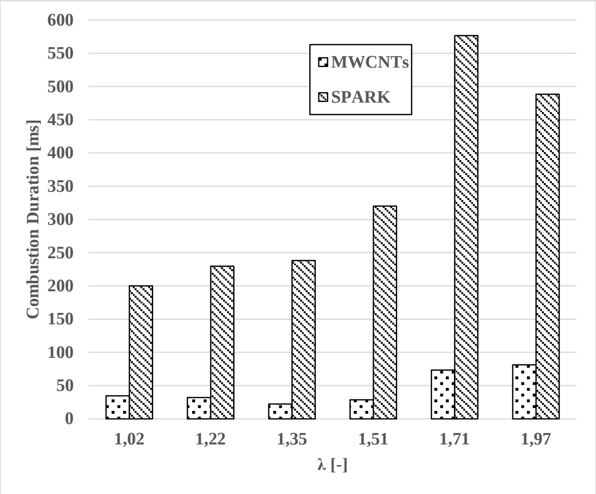

Fig. 6: Combustion duration for the MWCNTs photo-ignition and spark assisted ignition at λ ranging from 1 to 2

where Q is the heat released during combustion, γ is the specific heat ratio, equal to 1.38, V is the combustion chamber volume and p is the measured pressure.

Thanks to the calculation of the heat release rate, it is also possible to estimate the combustion duration, conventionally defined as the time interval between the two instants at which the 10% and the 90% of the total heat of combustion has been released.

In "Fig. 6" the combustion durations for different λ are compared using the two ignition systems. It can be seen that using the MWCNTs as ignition agents leads to a combustion sensibly shorter.

Finally, in "Fig. 7" and "Fig. 8" the cumulative of time histories calculated with "(2)" are plotted respectively triggering the fuel mixture with MWCNTs and with spark plug. The calculation was implemented only during the rising phase of the chamber combustion pressure, since, as previously seen, only that phase is representative of the combustion process development. The final value of the cumulative, therefore, is the total heat released during combustion. It can be seen that the total heat is higher if lower values of λ are used. Moreover, the combustion triggered by MWCNTs leads to total heat released higher than with spark plug.

IV. CONCLUSIONS

In this paper, an ignition system is proposed for an air/methane mixture, based on the exposition of multi wall carbon nanotubes (MWCNTs) to the flash of a camera.

In the methodology proposed here, MWCNTs containing the 75% weight of ferrocene have been used since their cost is notably lower compared to SWCNTs. The autoignition agents have been added inside an air/methane mixture afterwards exposed to a flash light pulse. The combustion process so realized has been compared with the one obtained with a traditional spark plug used in the spark ignition engines.

The experiments have been run, inside a constant volume combustion chamber, aiming at comparing the combustion process characteristics of an air/methane mixture enriched with MWCNTs and ferrocene samples, with the one obtained with the spark plug. During the tests 20 mg samples of MWCNTs and ferrocene with 1:3 ration have been used.

Dynamic pressure measurements show that the MWCNTs photo-ignition provides a more rapid rise in pressure and a higher peak pressure which corresponds to a higher het release than spark ignition.

Furthermore, high-speed camera images show that MWCNTs photo-ignition process results in distributed quasi-homogeneous ignition and a better consumption of the air/fuel mixture without the formation of a discernible combustion wave. This behavior is opposite to what observed with spark ignition, namely a single ignition point and flame propagation across the combustion chamber.

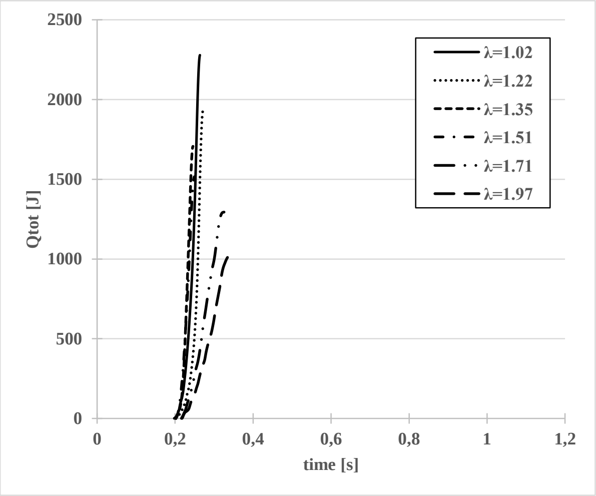

Fig. 7: Energy released for the MWCNTs assisted ignition at λ ranging from 1 to 2

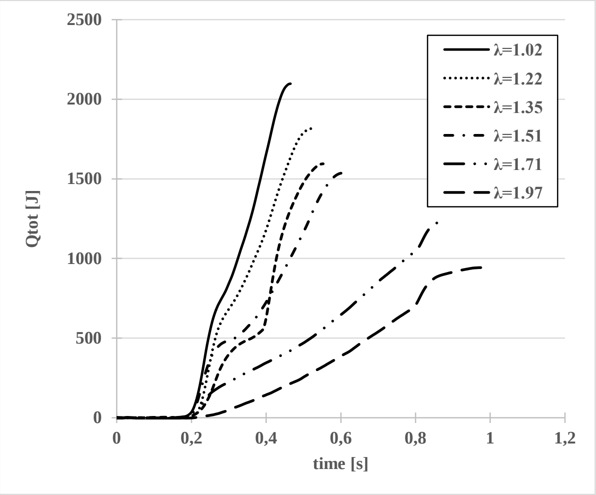

Fig. 8: Energy released as a function of time for the spark-assisted ignition at λ ranging from 1 to 2

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