

Review Article

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Light-Induced ignition of Carbon Nanotubes and energetic nano-materials: a review on methods and advanced technical solutions for nanoparticles-enriched fuels combustion

<https://doi.org/10.1515/rams-2020-0010>

Received Sep 09, 2019; accepted Jan 15, 2020

Abstract: Aim of the present manuscript is to provide an overview of all possible methods and light source typologies used by the different research groups for obtaining the energetic nano-materials' photo-ignition, showing the latest progress related to such phenomenon employing, also, alternative radiation sources to the common Xe lamp. In fact, the employment of a different source typology can open new usage prospects respect to those enabled by the Xe lamp, mainly due to its technological limitations. Therefore, several studies are faced to test light sources, such as lasers and LEDs, for igniting the nano-energetic materials (as CNTs mixed with metallic catalyzers, Al / CuO nanoparticles, etc); these nano-materials are usefully employed for starting, in volumetric and controlled way, the combustion of air-fuel mixtures inside internal combustion engines, leading to significant benefits to the combustion process also in terms of efficiency, reliability, and emissions of pollutants. Several research works are presented in literature concerning the ignition of liquid / gaseous fuels, without nano-particles, employing laser sources (i.e laser-based plugs in place of the common spark plugs); therefore, an innovative solution is proposed that employs multi-point laser-plugs for inducing the ignition of nano-materials dispersed into the air-fuel mixture inside the cylinder, so further improving the combustion of the fuel in an internal combustion engine.

Keywords: Light ignition, nano-particles, laser-plug, light absorption, internal combustion engine

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1 Introduction

The searching of new technical solutions for improving the efficiency of internal combustion engines represents a very attractive research field because they are omnipresent in every area of human activities; hence, the investigation on techniques and methods for optimizing the engine fuel consumption and reducing the emission of harmful pollutants is a topic more relevant than ever.

In the last decades, the employment of nano-scale materials for reaching these objectives was extensively investigated; specifically, the carbon nanotubes (CNTs) photo-ignition phenomenon could represent an optimal solution for the design of innovative fuels ignition systems inside internal combustion engine; as known, by exploiting CNTs photo-ignition as triggering agents for the liquid or gaseous fuels combustion, several improvements of the combustion process can be ensured, as a shorter combustion duration, a lower ignition delay and a higher peak of the internal pressure than those obtained with a common spark plug [1]. These results are commonly associated with a more distributed ignition within the combustion chamber of fuel mixture, ascribable to multiple ignition nuclei distributed inside it.

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However, many technical challenges are actually addressed by the interested research groups for enabling the real implementation of ignition systems based on the photo-ignition phenomenon; in particular, the main problem that has to be faced regards the light source typology employed to induce the combustion starting. In literature, most of the proposed works are related to the photo-ignition of CNTs mixtures through a Xenon lamp; nevertheless, it presents numerous technological limitations, as short life-time, intrinsic mechanical instability, low operating frequency, making it not of real applicability in an internal combustion engine [2]. In the last years, several studies are carried out for testing alternative light sources (namely, Light Emitting Diode-LED and Light Amplification by Stimulated Emission of Radiation-LASER), for inducing the photo-ignition process of energetic nano-materials often mixed with metallic precursors, that structurally are more suitable for an automotive application [3–14]. In fact, the application in which the photo-ignition phenomenon is exploited is determined also by the typology of light source employed to trigger the fuels combustion.

This manuscript aims to provide an overview of all possible methods and technologies used by the different researchers to obtain the energetic nano-particles (NP) or nano-materials photo-ignition. As aforementioned, Xenon lamp was the first source employed for performing photo-ignition tests on energetic nano-materials but actually LED sources are under investigation, to understand if they can be employed in automotive applications, as well as lasers are widely tested, for representing both more suitable alternatives to the Xe lamp. Also, the laser-induced ignition of air-fuel mixtures inside a combustion chamber ensures several benefits on combustion process, such as no quenching of the combustion flame kernel, more spatial control on ignition area inside the engine cylinder, the possibility of inducing a multi-point ignition, as well as a greater control of the ignition time [5]. By using laser-based ignition systems, all these benefits could be exploited for improving the engine efficiency and reliability particularly when lean air-fuel mixtures are employed, thus, allowing to save in fuel consumption and to reduce the emissions of the exhaust gases. Hence, this technology can represent an important approach for reducing the environmental impact caused by the continuous combustion of fossil fuels in power plants and vehicles, enabling the reduction of pollutant levels released in the atmosphere.

Therefore, the employment of laser sources to start fuel combustion inside the engine cylinder, without the use of photo-ignitable nano-particles, is investigated by different researchers and automotive companies. By

means of very short laser pulses (time duration of the order of nano-seconds), directed through a suitable optical section inside the engine cylinder, the combustion of different gaseous fuels as following reported can be induced, leading to significant benefits to the combustion in terms of efficiency and reliability [3–14]. In addition, the development of laser sources featured by small dimensions and able to be easily installed on the engine simply retrofitting for the classical spark plugs and capable to operate in harsh conditions (*i.e.* high vibrations and temperatures) was a technological challenge of the recent years; as detailed below, nowadays several laser-based plug igniters have been realized and commercialized.

The remainder of manuscript is structured as follows: in the second paragraph, the research works, previously cited, focused on the nano-materials' photo-ignition by using different typologies of light sources (as Xe-lamp, LED and LASER) are discussed; afterward, in the third paragraph, the last experimental results regarding the combustion of different fuels enriched with energetic NPs are shown, also comparing our previously obtained results with those reported in the literature. The fourth paragraph reports an overview of recent developments relative to the laser-induced combustion of gaseous mixtures or spray of liquid fuels by using a laser plug, in place of traditional spark plugs applied to the engine cylinders. Finally, future developments and conclusions are reported in the last paragraph; in particular, an innovative solution that integrates multi-point laser plugs with the addition of photo-ignitable nano-materials dispersed into the cylinder is proposed. This solution promises to enhance the fuel combustion process into an internal combustion engine, concerning the actually reached results.

2 Research works focused on CNTs / nano Energetic Materials / nanoparticles photo-ignition

Numerous research works deal with the photo-ignition of CNTs or other nano-particles typologies by using a laser as a light source or other trigger source typologies such as thermal heat sources [15–20]. For instance, the photo-initiation of *As-Prepared SWCNTs* (APSWCNTs), using a laser, was examined in [15]; the researchers also used ferrocene for enhancing the photo-ignition reaction. Various ratios of nanotube/ferrocene were examined and it was determined that a 1: 2 ratio was optimal for laser initiation of the samples. Laser initiation was performed by using dif-

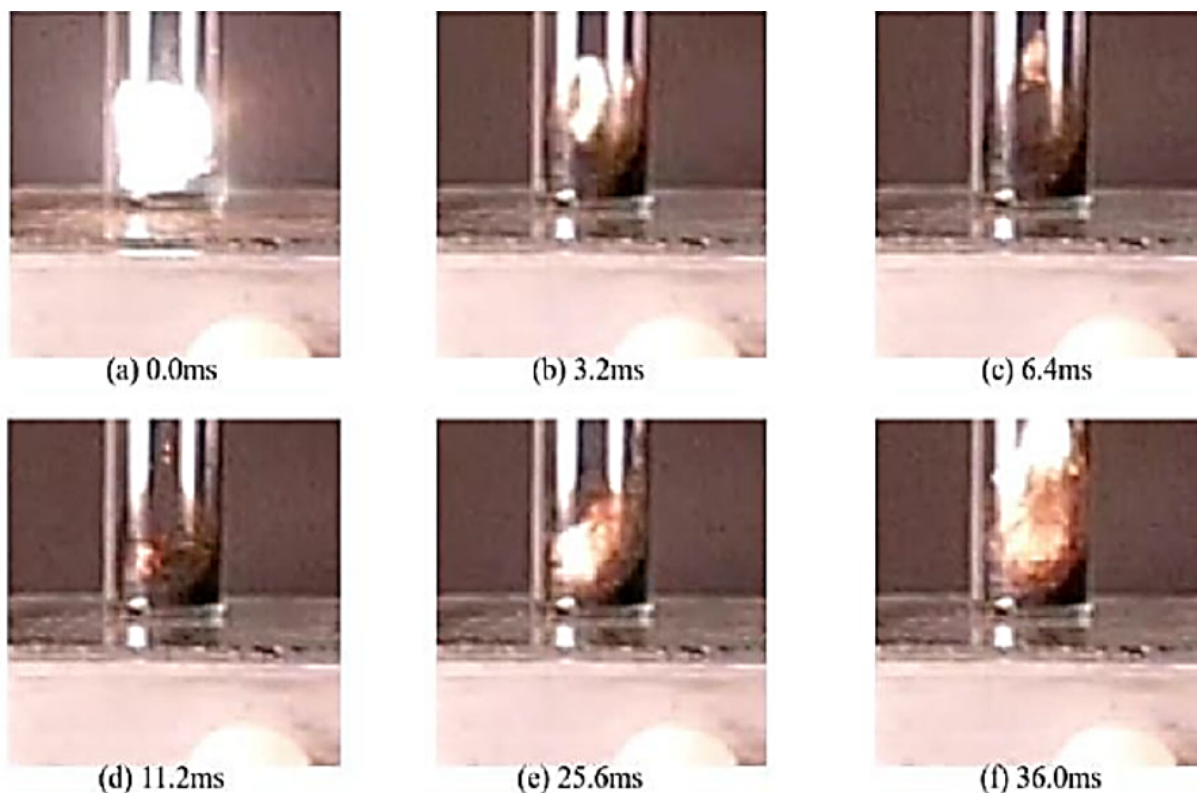


Figure 1: High-speed camera photos, provided by the authors, of the laser initiation of APSWCNT/ferrocene (1:2, 10 mg total) displaying the initial ignition (a-d) followed by a secondary ignition (e-f) when the ferrocene is initiated and oxidizes. Time shown refers to the amount of time passed since the light source was triggered [15].

ferent wavelengths of the emitted light beam, thus finding a higher sensitivity of the tested samples at 532 nm. Several brands of SWCNTs were investigated and comparisons were made between their reactions as a function of the residues of metal catalyst and weight percentage. The APSWCNT/ferrocene (1:2, 10 mg) samples were prepared in a glass sample vial, as shown in Figure 1, and ignited by means of the laser (single pulse with energy equal to 152 mJ); hence, the authors used a pyrometer to record the temperature of the tested samples. The APSWCNT samples completed the reaction within 0.5 ms but, with ferrocene present, the authors found that the sample burned for about 150ms; ferrocene was initiated without nanotubes (*i.e.* after about 25ms of the light pulse). Therefore, a secondary peak was observed around 25ms; for the authors, this could be due to the ferrocene being ignited and oxidizing from the initial nanotube absorption [15].

The combustion time duration ranged from 80 ms to 200 ms, being the entire reaction completed in less than 200 ms; the addition of ferrocene determined a higher initial temperature inside the sample and a much longer burning time, as illustrated in Figure 2. The used laser source was a *Continuum Surelite III Nd:YAG* (wavelength

1064 nm, 10 Hz repetition rate, 5 ns pulse duration); a 4 mm diameter laser spot size was irradiated on the sample and a single pulse was used. The experiments were performed by using a pulse energy equal to 152 mJ for ensuring reproducible results without using too much energy; this energy corresponds to a power density of 2.42×10^9 W/cm² [15].

After ignition, the sample shows large areas of orange color, due to the oxidation of the iron from ferrocene to Fe₂O₃ and traces of Fe₃O₄ as illustrated in Figure 1 and already reported in [21], but also in our carried out research works [1, 22].

In Ref. [16], the authors analyzed the effects on the combustion and explosion parameters of nano-energetic materials due to the addition of MWCNTs ignited by laser irradiation (as illustrated in Figure 3); the researchers demonstrate that the ignition power threshold and ignition delay gradually decreased by increasing the MWCNT content inside the tested samples, *i.e.* Al/CuO nanoparticles (NP). In the experimental tests, the power threshold and ignition delay of MWCNT (10 wt%)/Al NP/CuO NP decreased by ~40% and ~50%, respectively, compared to those of MWCNT (0 wt%)/Al NP/CuO NP samples; this in-

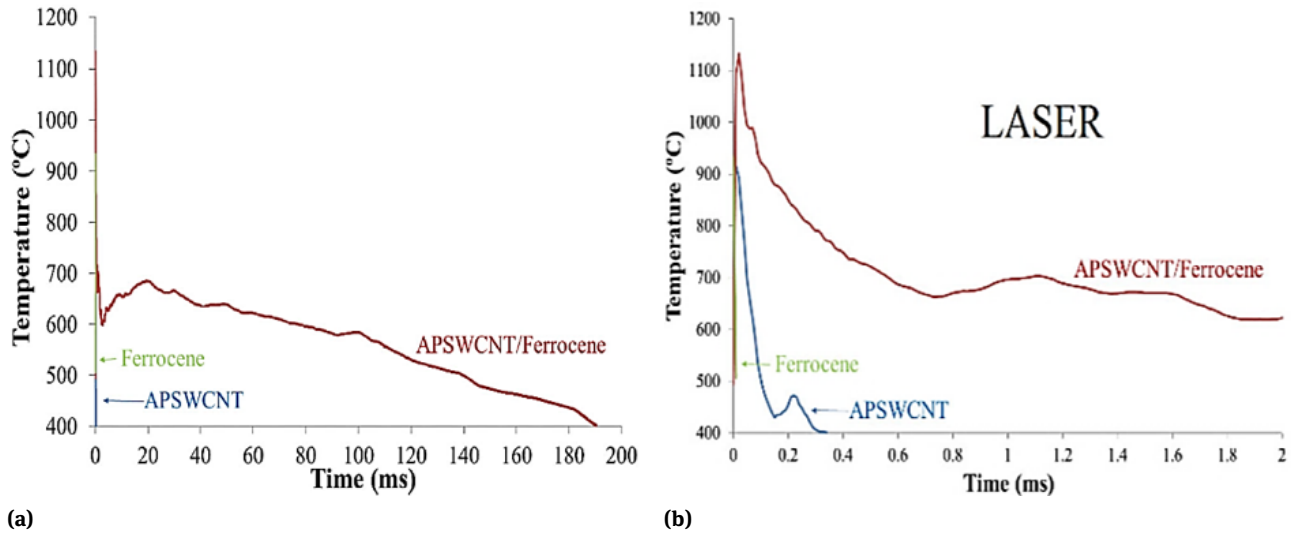


Figure 2: Laser initiation of APSWCNT/ferrocene (1:2, 10 mg) sample, with a pulse energy of 152 mJ (a) and view of the expanded short time region (from 0ms to 2ms) (b) [15].

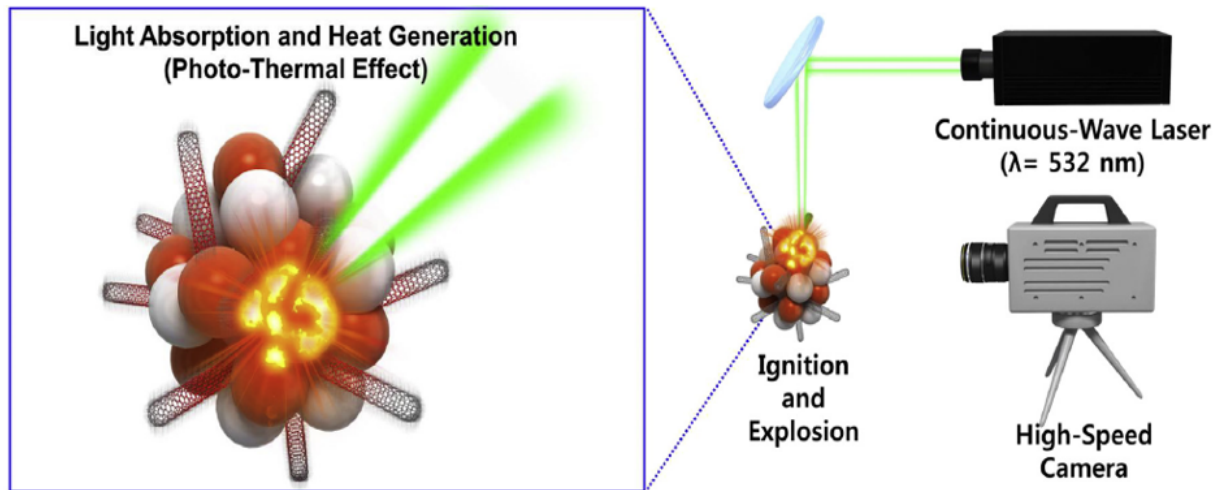


Figure 3: Schematic view of laser ignition experimental test, carried out by the authors in [16] by using *MWCNT/Al NP/CuO NP* samples.

indicates that MWCNTs acted as optical igniter of the nano-material. In fact, the laser beams were absorbed by the MWCNTs with consequent generation of heat local spots, that promote the nano-energetic material's ignition, as also reported in our previous work [22]. Furthermore, the authors demonstrate that by adding to the nano-energetic materials matrix an optimal amount of 2 wt% MWCNTs, the pressurization rate, flame propagation speed, and pressure wave speed during the combustion process were enhanced [16]. Specifically, several MWCNT (0, 1, 2, 5 and 10 wt%)/Al/CuO samples were tested by recording the ignition and combustion processes by means of a high-speed camera (Model *FASTCAM SA3 120 K*, *Photron*) with

a frame rate of 30 kHz, which usefully allows to highlight the differences in the initial moments of the ignition.

A *pressure cell tester (PCT)* was employed for measuring the pressure transient of *MWCNT/Al NP/CuO NP* composites and, in addition, to evaluate the contribution of MWCNTs in the *Al NP/CuO NP* combustion process. The researchers performed a series of tests by exposing composite powders to laser irradiation; in particular, a CW (continuous-wave) green laser beam (wavelength equal to 532 nm, power interval [0-1286mW], beam diameter equal to 2.5 mm, Model *SDL-532-1000T*, *Shanghai Dream Lasers Technology*) with different intensity levels was employed. The experimental results demonstrate that the laser ignition threshold power decreased as a ~2 wt% MWCNTs per-

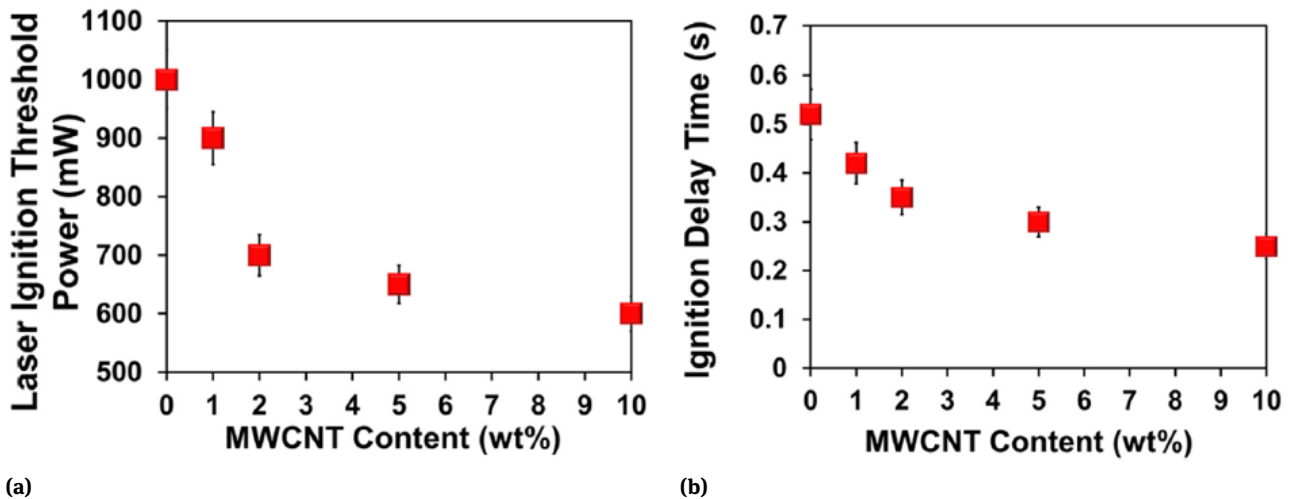


Figure 4: Laser ignition power thresholds as function of MWCNT weight ratio in *Al NP/CuO NP* composite samples (a), and ignition delay of *MWCNT/Al NP/CuO NP* sample depending on the MWCNT weight ratio (b) [16].

centage was added to the *Al NP/CuO NP* matrix, as reported in Figure 4a. This indicates that, for inducing the ignition of composite powders containing higher MWCNTs amount, a lower-power laser beam is needed; moreover, by increasing the amount of MWCNT to ~ 2 wt% in the *Al NP/CuO NP* matrix, also the ignition delay time is decreased, as illustrated in Figure 4b. According to the authors, this is due to the MWCNTs in the *Al NP/CuO NP* matrix, that promote, by the photo-thermal effect, a rapid local ignition of *MWCNT/Al NP/CuO NP* composites. However, by further increases (>2 wt%) of the MWCNTs content, the power threshold, and delay time of laser ignition are less affected. In fact, a MWCNTs' excessive content improves the heat dissipation to the environment caused by the rapid heat transfer to entangled MWCNTs, thus, deteriorating the photo-thermal effect. Therefore, concluding their research work, the authors established that MWCNTs can potentially be used as optical igniters and explosion control media for realizing a remotely-controlled laser-based ignition / detonation system based on *Al NP/CuO NP* nano-energetic materials [16].

In Ref. [17], the authors used a conventional camera flash to photo-ignite *Fe* nano-particles (NPs) analyzing in detail the obtained photo-ignition process; at first, an initial ignition stage featured by 2000 K maximum temperature takes place and, subsequently, there is the burning stage featured by an 800 K temperature. The microstructure characterization indicated evident oxidation of the *Fe NPs* to Fe_2O_3 and that increasing the *Fe-NP* amount lower minimum ignition energy is required to ignite the compound, which could be due to the enhancement of

the light absorption. The authors found that, when the samples have the same diameter, the larger mass could increase the particles number per unit area and therefore the energy absorption which results in a lower Minimum Ignition Energy (MIE). When the samples with the same mass were prepared, the samples with NPs' larger diameter lead to a lower particles concentration and higher MIE. The high temperature for inducing the ignition was attributed to the huge energy released by the flash; subsequently, the temperature decreased due to the energy released by the *Fe-NPs* oxidation. The authors obtained the *Fe NPs* photo-ignition with a MIE value of $246 \text{ mJ}/\text{cm}^2$ with a distance lamp-sample of about 1 mm (the *Fe NPs* were packed into a cylindrical shape and placed on a 1mm-thick glass slide above the xenon flash tube in the air). In our experimental tests, the distance lamp-sample was equal to 4mm for all the tested samples, obtaining a MIE value (in the case of MWCNTs:ferrocene ratio of 4:1) of $51.37 \text{ mJ}/\text{cm}^2$; it was concluded, by the authors, that flash can elevate the *Fe NPs* temperature to a very high level, which exceeds the ignition point of *Fe NPs* a lot [17].

In Ref. [18], the ignition and reaction characteristics of aluminum nano-composite thermites enriched with copper oxide oxidizers were studied. The authors found that Cu_2O (*cuprous oxide*) releases oxygen around 200 K higher than CuO (*cupric oxide*), but ignites at the same temperature as the other oxidizer. In particular, Cu_2O was synthesized with dimensions from 200 to 1500 nm and tested with temperature jump (T-jump) heating of $>105 \text{ K/s}$ for oxygen release and ignition with nano-aluminum, whereas CuO systems have many similar properties but

produce more intermediate (O_2) and equilibrium (Cu) gases. Therefore the researchers obtained that both oxides ignite through a condensed phase mechanism independent of gaseous oxygen.

Authors in [19] investigated about under-water ignition of nanoscale-Energetic-Materials (nEMs); because the water affects the reactants before the ignition and also dampens the subsequent combustion reaction, the nEMs under-water ignition is a challenge. In their work, the researchers demonstrated a viable method for synthesizing *Sea Urchin-Like Carbon Nanotube (SUCNT)/nEM* composite pellets coated with a thin film of a hydrophobic polymer; by using them, an underwater ignition and following explosion can be obtained. The absorption of the flash's light energy rapidly converts it into thermal energy; afterwards, this energy is then properly focused to trigger the ignition reaction of the core catalysts and adjacent nEMs. Flash-induced burning tests indicated the importance of the *SUCNTs* dispersed in the nEM matrix for the flash ignition and subsequent underwater explosion. However, the authors verified that the heat energy generation and burning rate of *SUCNT/nEM* composites could be reduced by adding an excessive amount of *SUCNTs* in the nEM matrix because they cause both a more rapid dissipation of heat to the surrounding environment and physico-chemical intervention in the reactants. Therefore, by embedding the specially designed *SUCNTs* into nEM pellets, the authors obtained nEM composite powders and pellets which can be photo-ignited by a Xenon flash and underwater explosion reactivity is also obtained [19].

In Ref. [20], the authors analyzed the effect on the ignition and combustion properties of Al/CuO NP compounds enriched with *Carbon Black Nanoparticle (CB NP)*. In particular, the role of *CB NPs* as a heat transfer medium in the nEM compound, ignited with different thermal heat sources, in place of an external light source, was evaluated; as a potential strategy to improve the heat transfer parameters of *Al-based nEMs*, the addition of *CB NP* to nEM matrix was considered. The *CB/Al/CuO NP* composite powders were synthesized by sonication in *EtOH* solution, with subsequent by solvent evaporation; the experimental tests demonstrated that by adding less than 1wt.% of *CB NPs* in the *Al/CuO NP*-based nEMs the pressurization and burning rates were enhanced because the heat transfer in the combustion reactions was improved. However, an excessive *CB NPs* (> 1 wt.%) amount added to the *Al/CuO NP*-compound heavily deteriorated the combustion and explosion processes, because of a more rapid heat dissipation to the environment. Moreover, by adding *CB NPs* in the nano-energetic matrix, the ignition time delay was reduced, given the improvement of the com-

pound thermal properties; therefore the *CB NP*-based additives can represent a useful tuning factor, for affecting the thermo-chemical interactions and thermal properties of nEM compounds, thus, enabling a regulation of nEMs ignition and combustion properties in several applicative scenarios [20].

Before to analyze the research works of literature related to the last innovative applications of nano-particles photo-ignition, particularly focused on the automotive field, the following Table 1 summarizes the results related to the *CNT* photo-ignition power/energy thresholds reported in our previous works and a comparison between the obtained results and those of the other research works discussed above. The *CNT* ignition was induced through a CW Xe lamp, also a pulsed Xe lamp and, finally, by using LED-based sources (similarly, CW and pulsed sources were considered). In Table 1, for different light source typologies (*i.e.* Xe lamp, LED source and laser source) both in CW and pulsed emission, the ignition time delay and the power/energy thresholds for photo-igniting the considered nEM are reported. Relatively to our results reported in the table, in case of CW Xe lamp, ignition threshold was reduced by increasing the concentration of metallic catalyzer in the sample [22]; by comparing the results obtained through a CW Xe lamp and those obtained with a LED sources, as reported in our previously published research work [1, 2, 22, 23], it is possible to notice a reduction, from 20% up to 40%, of the ignition thresholds, for all the considered compositions, by enriching with porphyrin powder the samples [24]. Furthermore, for extracting useful information relative to the minimum ignition energies and time delays of the ignition process, high-definition videos were acquired during every ignition test. These energy values were then compared, showing an optimal agreement, with analogues results obtained during the single-pulse experimental tests carried out employing a LED source; the obtained MIE values show a similar trend, depending of the sample weight ratios, compared to our similar results obtained by using a pulsed Xe lamp [1, 2, 23, 25], but with higher values given the lower luminous power emitted from the LED source compared to those produced by Xe lamp. Further improvements related to the optical sections of collimation and focusing have to be faced for reaching higher light power density from the LED source, with the aim of reducing the MIE values. Ignition thresholds, relative to laser-induced ignition are also reported in Table 1; as it is possible to notice, higher luminous intensity is required to photo-ignite *MWCNT/Al NP/CuO NP* compounds and also a greater ignition time delay [17] compared to those obtained by using *MWCNTs:ferrocene* and LEDs light source. With *AP-*

Table 1: Results related to the nano-particles photo-ignition process, by using Xenon lamp, LEDs and laser, obtained by the carried out experimental tests in our research activities and by other research works.

| | <i>Our published results</i> | | <i>Literature results</i> |
|--|--|--|--|
| | <i>Continuous Wave/Emission lamp</i> | | |
| | <i>Xenon-lamp solution</i> | <i>LED solution</i> | <i>Laser solution</i> |
| Luminous Power needed to obtain ignition | MWCNTs:Ferrocene (1:3) (Entire spectrum of the Xe lamp) 377mW [mW/cm²] [8] MWCNTs:Ferrocene (1:3) (UV region selected) 330 [mW/cm²] [8] | MWCNTs:Ferrocene (1:3) 266 [mW/cm²] [24] | MWCNT/Al NP/CuO NP composite powders 600mW [16] |
| Ignition delay time | < 100ms | 110ms | 250ms [16] |
| | <i>Pulsed lamp</i> | | |
| | <i>Xenon-lamp solution</i> | <i>LED solution</i> | <i>Laser solution</i> |
| | MWCNTs:Ferrocene (4:1) 51.37 [mJ/cm²] [9, 10] | MWCNTs:Ferrocene (4:1 and 2:1) 266 [mJ/cm²] [24] | APSWCNT:ferrocene (1:2) 152 mJ [15] 2.42×10⁹ W/cm² [15] |
| | – | MWCNTs:Ferrocene (2:1) (samples enriched with porphyrin) 153 mJ/cm² [24] (180 mW/cm²) | <i>Xenon lamp solution</i> Fe NPs 246 mJ/cm² [17] |
| Ignition delay time | ≈ 2 ms | 110 ms | 0.5 ns [15] 5 ns [17] |

Table 2: Changes in the Engine Performance and Emissions of Biodiesel Fuel [37].

| Additive | Dosing Level | Torque Increase | Brake Power Increase | CO Reduction | CO ₂ Increase | NO _x Reduction | Cost (\$/Liter) |
|----------|--------------|-----------------|----------------------|--------------|--------------------------|---------------------------|-----------------|
| MgO | 25 ppm | 2.3% | 2.4% | 3.4% | 7% | 2.2% | 0.015 |
| MgO | 25 ppm | – | – | 10.4% | 2% | 0.4% | 0.020 |

SWCNT:ferrocene mixture and laser as light source, the energy threshold obtained by researchers was equal to 152 mJ with a power density of $2.42 \times 10^9 \text{ W/cm}^2$, much higher than that obtained by using LEDs (180 mW/cm^2) [15, 24].

3 Innovative applications of the nano-materials to lubricants and coolants for automotive applications

Besides the use of nano-materials as fuels additives for improving the combustion performances and reducing the pollutants emission from the internal combustion engines,

as discussed below, the nanotechnologies find wide application also in other fluids employed in automotive applications, related either to the engine operation or to other mechanical parts of the car. Specifically, the main applications of nano-materials as additive of advanced lubricants, or cooling liquids, for making them more efficient and performing, applied to the automotive field are following reported. Indeed, the high surface area ratio of the nano-material can be used for catalyst functions for fastening the chemical reactions or for improving interracial driven phenomena. For these reasons, the nano-materials are commonly dispersed in liquid media for improving its thermal properties or its tribological performances.

The nano-coolants are an innovative solution for improving the heat transfer capability of a cooling liquid, by means of the diffusion inside a media fluid of nanopar-

Table 3: Table reporting the improvements of fuels combustion deriving by the use of the nano-particles photo-ignition in place of the traditional spark-plug for CH₄, LPG and H₂ [2].

| Gaseous fuel | Air-fuel equivalence ratio λ [-] | Trigger system | Ignition delay [ms] | Combustion duration [ms] | Combustion peak pressure [bar] |
|-----------------|--|-----------------------|---------------------|--------------------------|--------------------------------|
| CH ₄ | $\lambda = 1.00$ | MWCNTs photo-ignition | 38 (-27%) | 25 (-22%) | 20.5 (+7%) |
| | | SPARK-PLUG | 52 | 32 | 19 |
| | $\lambda = 1.25$ | MWCNTs photo-ignition | 40 (-27%) | 32 (-36%) | 17 (+6%) |
| | | SPARK-PLUG | 55 | 50 | 16 |
| | $\lambda = 1.5$ | MWCNTs photo-ignition | 50 (-30%) | 45 (-29%) | 15 (+1%) |
| | | SPARK-PLUG | 72 | 64 | 14.8 |
| | $\lambda = 1.75$ | MWCNTs photo-ignition | 70 (-30%) | 74 (-17%) | 12.7 (+5%) |
| | | SPARK-PLUG | 100 | 90 | 12 |
| | $\lambda = 1.98$ | MWCNTs photo-ignition | 95 (-36%) | 81 (-54%) | 10.5 (+5%) |
| | | SPARK-PLUG | 150 | 177 | 10 |
| LPG | $\lambda = 1.00$ | MWCNTs photo-ignition | 27 (-50%) | 21 (-43%) | 23 (+9.5%) |
| | | SPARK-PLUG | 55 | 37 | 21 |
| | $\lambda = 1.25$ | MWCNTs photo-ignition | 45 (-42%) | 38 (-33%) | 19.5 (+7%) |
| | | SPARK-PLUG | 78 | 57 | 18.2 |
| | $\lambda = 1.5$ | MWCNTs photo-ignition | 67 (-40%) | 50 (-43%) | 17 (+0%) |
| | | SPARK-PLUG | 112 | 88 | 17 |
| | $\lambda = 1.75$ | MWCNTs photo-ignition | 98 (-32%) | 68 (-44%) | 14.8 (-0.6%) |
| | | SPARK-PLUG | 144 | 123 | 14.9 |
| | $\lambda = 1.98$ | MWCNTs photo-ignition | 108 (-31%) | 79 (-40%) | 13.5 (-8%) |
| | | SPARK-PLUG | 158 | 132 | 14.7 |
| H ₂ | $\lambda = 1.00$ | MWCNTs photo-ignition | 12 (-33%) | 5 (-37%) | 25.3 (+11%) |
| | | SPARK-PLUG | 18 | 8 | 22.7 |
| | $\lambda = 1.25$ | MWCNTs photo-ignition | 13 (-48%) | 6 (-40%) | 22.5 (+7%) |
| | | SPARK-PLUG | 25 | 10 | 21 |
| | $\lambda = 1.5$ | MWCNTs photo-ignition | 15 (-60%) | 7 (-63%) | 21.6 (+8%) |
| | | SPARK-PLUG | 38 | 19 | 20 |
| | $\lambda = 1.75$ | MWCNTs photo-ignition | 18 (-65%) | 10 (-81%) | 17.5 (+3%) |
| | | SPARK-PLUG | 52 | 53 | 17 |
| | $\lambda = 1.98$ | MWCNTs photo-ignition | 19 (-66%) | 13 (-80%) | 16 (+3.2%) |
| | | SPARK-PLUG | 56 | 67 | 15.5 |

ticles, typically, metals, metal oxides, CNTs or other carbides. Usually, they are classified in the following categories: metallic, metallic and not-metallic oxides, nanodroplet and carbon nanotubes nano-coolants [26]. The main application fields of such fluids concern automotive, food and industrial plants, electronic device cooling and renewable energies; in all these fields, a cooling liquid able to convey a higher heat flux allows to use a cooling system with lower dimensions and cost.

In Ref. [27], the authors carried out a comparison, in terms of convective heat transfer capability, of Al₂O₃/water nano-fluid and pure water when the liquids were forced in an automobile radiator, constituted by 33 vertical tubes with elliptical cross-section, that were immersed in a cross airflow in steady regime with flow rate variable in the range from 3 to 8 LPM (liters per minute, l/min). Specifically, the authors considered five Al₂O₃/water nano-fluid samples with different concentrations (from 0 up to 1.0 Vol%). Experimental tests indicate

that, for low nano-particles concentration, the heat transfer efficiency of the nano-fluid increases up to 40-45% compared to the pure water.

In Ref. [28], the authors compared the thermo-physical parameters of different typologies of nano-fluids, both water-based and glycol-based, for determining the nano-fluid typology with the best cooling performances. Both base fluids (*i.e.* water and ethylene glycol) were mixed with CuO and Al₂O₃ nanoparticles for obtaining the desired nano-fluid. As reported in [29], by adding nanoparticles to a base fluid, an improvement of thermophysical properties, in terms of thermal conductivity, thermal diffusivity, thermal viscosity, and convective heat transfer coefficient, compared to base fluids, is obtained. The authors derived equations describing the behavior of the nano-fluid in a radiator and solved them numerically by Rouge-Kutt and linear shooting methods. Specifically, the simulations demonstrate that CuO-based nano-fluids show much better heat transfer properties compared to Al₂O₃-

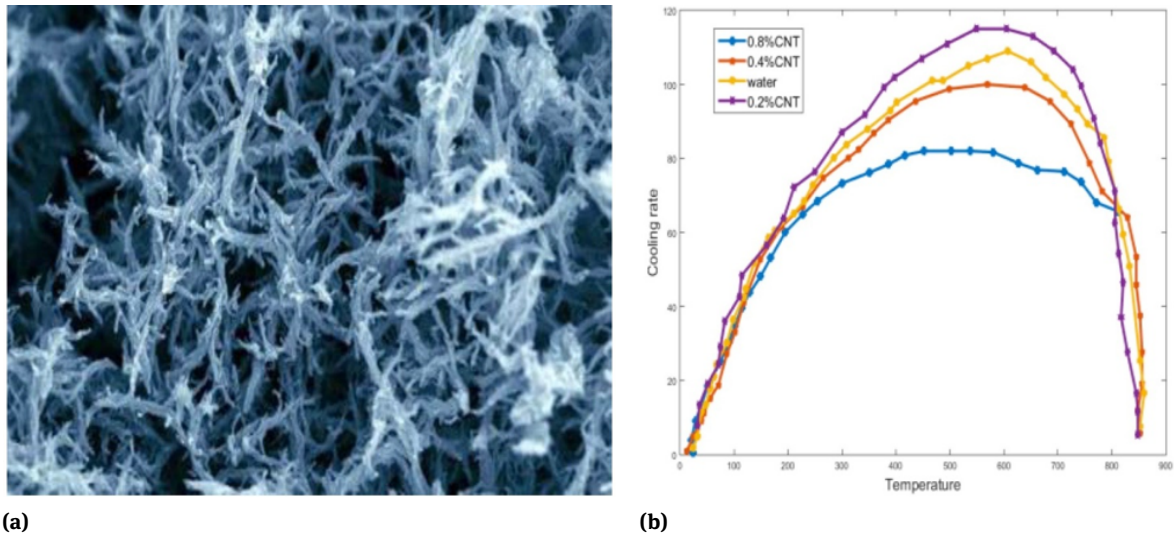


Figure 5: SEM image of the water-based CNTs nano-fluid (a); cooling curve of the temperature probe material quenched by the nano-fluid (25°C initial temperature) with different CNTs concentrations, considering the water as reference liquid (b).

based nano-fluids. In addition, a higher ability to remove and conduct the heat by a radiator was obtained for CuO-Ethylene glycol nano-fluid. For all considered nano-fluids, the thermal conductivity improves by increasing the nanoparticles' amount.

Liu *et al.* [30] compared the heat transfer performances of water-based CNTs nano-fluid with those of the classic cooling water, employed in a cooling system of a six-cylinders diesel engine. The preparation of water-based CNTs nano-fluid was performed by adding to water the CNTs, according to the desired concentration, and the SDBS dispersant, for improving the dispersion of the nano-materials inside the fluid medium. Following, the CNTs suspension undergoes to sonication for obtaining the nano-fluid. In Figure 5a, the SEM (scanning electron microscope) image of the water-based CNTs nano-fluid is reported; from it, the efficient spatial dispersion of the nanotubes inside the fluid medium can be verified. A probe material, represented by 45 sheets of steel with dimension $20\text{ mm} \times 40\text{ mm}$ with a NiCr-NiSi (type K) thermocouple located to its center, was used for evaluating the cooling performances of the nano-fluids. Thus, after the heating of probe to 850°C for 10 minutes, this last is cooled in the nano-fluid (25°C initial temperature) for different CNT concentrations. The quenching capability of the nano-fluid with different concentrations is a measure of the cooling characteristics for the internal combustion engine. The cooling curve of the probe material within the nano-fluid with different CNTs concentrations, considering as reference liquid the water, is reported in Figure 5b; as evident,

the cooling capacity of the nano-fluid with low content CNTs (0.2%) is higher than nano-fluids with high CNTs content (0.8% or 0.4%), as well as heat transport capability of high CNTs content nano-fluids is worst compared to the water one.

As previously discussed, the addition of nanoparticles to a generic lubricant can enhance its lubricant performances, allowing to reduce the friction and wear between contact surfaces. For these reasons, several research works are reported in the literature concerning the beneficial effects of the nano-particles dispersed into lubricant for reducing the friction and wear rate. However, several factors, such as size, shape, volume ratio of nanoparticles enriching the lubricant, can affect the coefficient of friction (COF). In Ref. [31], the authors investigated the effects on COF of different boric acid and copper nanoparticles concentrations [with ratios 1:10, 2:10 and 3:10], both in engine oil SAE 15W40 and SAE 90 transmission oil, employed to lubricate cast iron and case carburized EN 36 steel. They demonstrated that for both considered additives, the coefficient of friction is reduced, in case of transmission oil on the carburized surface, given the increasing of pressure contact and the flattening of nanoparticles between the contact, reducing the friction and wear. Wu *et al.* [32] evaluated the effects on the COF and mechanical wear of both API-SF oil and base oil, after the addition of CuO, TiO_2 , and nano-diamond nanoparticles. They demonstrated that all considered nanoparticles led to a reduction of COF and improvement of anti-wear properties, when used as additives of lubricant oils; specifically, for CuO nanoparticles added

to SF oil a reduction of the COF from 18.4% to 5.8% was obtained compared to the oil with no additives. The authors explained such reduction with the viscosity effect in low temperature regime and the rolling effect in high temperature regime. Considering anti-wear tests, a reduction of worn scare depths of, respectively, 16.7% and 78.8% for SF oil and base oil both enriched with CuO nano-particles, than not-additived oils was observed; such reductions are ascribable to CuO nanoparticles deposited on the worn scar, that decrease the shearing stress, improving the tribological properties.

In Ref. [33], graphene (Gr) nano-lubricant was proposed for improving the COF and wear behaviors of mechanical components for automotive applications. A commercial lubricant oil (Castrol EDGE professional A5 - 5W-30) was employed as reference oil, to which the graphene nano-particles were added in different concentrations (*i.e.* 0.03%, 0.2%, 0.4%, and 0.6% wt.), for avoiding the nano-material sedimentation in the base fluid. The evaluation of the tribological properties was performed using a tribometer based on ASTM G181 test method and by an AVL dynamometer under NEDC (New European Driving Cycle), for linking the tribological performances with the engine performances. Experimental tests demonstrated, that by using Gr-enriched nano-fluids, improvements of anti-friction and anti-wear performances, compared to the reference oil, in the range of 29 - 35% and 22 - 29%, respectively, were obtained. Furthermore, by using the AVL dynamometer, an increase of engine's torque and power between the 7 and 10%, under different load and speed conditions, were verified and, consequently, a 17% decreasing of fuel consumption was obtained.

In this context, the main issue that has to be faced is to keep in suspension the nano-particles inside the base fluid; in fact, particles aggregation heavily limits the lubricant capability of the lubricant liquid. For this reason, different strategies are implemented for improving the dispersion of the nano-materials, which require the use either of dispersants or surface modifying agents. Chen *et al.* [34] examined the effects of typology, size and surface modification of nano-particles on the dispersion capabilities of the nano-material in the base fluid. In particular, they demonstrated that surfactant agents are indicated for nano-particles with size under 50 nm, whereas for large nanoparticles (>50 nm), the alkoxysilanes are the best solution; finally, surface silanization turned out to be the best solution for dispersing metal oxide nanoparticles with size higher 10 nm, given its higher grafting density.

4 Last experimental results related to the combustion of fuels enriched with nanoparticles

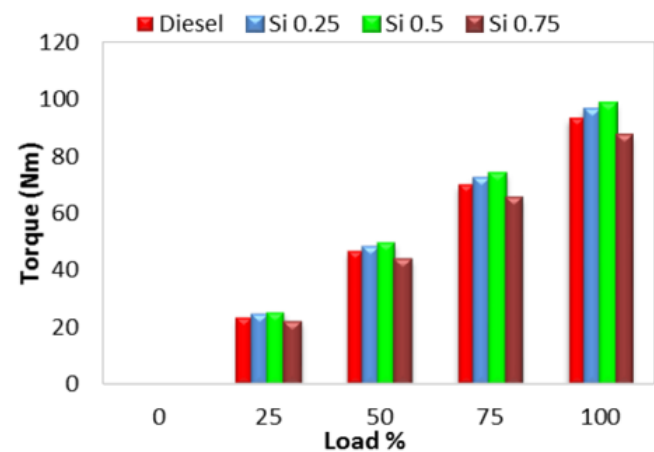
Several studies are facing the development of new technologies and strategies to make vehicles more even eco-compatible and eco-sustainable such as hybrid or electric propulsion, fuel cell, etc. However, it is difficult to replace all conventional gasoline vehicles with clean vehicles immediately, because of the costs of clean vehicles and energy sources, vehicle's performances, fuel-cell lifetime, etc. Therefore, several efforts are faced to improve the efficiency of the internal combustion engines and reduce the emissions harmful pollutants, CO₂, NO_x, etc.

Many research studies focus on the analysis of several ignition methods relative to the gaseous-fuel combustion; obviously, the most popular is the electric spark igniter even if a high-voltage circuitry and a high-power source are needed to allow its operation; in addition, a spark-plug is an intrinsically single-point ignition method, that prevents an optimal ignition of the air-fuel mixture inside a combustion chamber. Alternative ignition techniques as flame jet initiation and plasma jet injection, are very expensive, heavy, bulky and energy-intensive to operate [35]. Other ignition methods are based on the usage pyrophoric charges, obtained by mixing hypergolic propellant components, or through the activation of catalytic bed, requiring the usage of hazardous substances and/or complex/expensive materials or sophisticated reactors and mixing devices [35].

Researchers in Prof. Xiaolin Zheng's laboratory have designed and realized a low-power, high efficiency, homogenous photo-thermal fuel ignition technology based on simple nano-particle fuel additive [36]. Initially, it employed aluminum nano-particles (*Al NPs*), enabling a volumetric combustion through a flash-lamp in place of igniters based on sparks and hot-wire. This concept could also be expanded to other energetic thermites and mixtures with micro-particles. The nano-particle system can be easily installed in existing combustion engines and it is compatible with solid, liquid or gaseous fuel. The invention can reduce pollution and ignition delays in a variety of settings, particularly in rapid reciprocating combustion engines and supersonic combustors [36]. T. Özgür *et al.* have analyzed the addition of oxygen-containing nanoparticles to biodiesel, evaluating the effects on fuel properties, and exhaust emissions of the diesel engine [37]. SiO₂ and MgO NPs were dispersed into the fuel with concentrations of 50 and 25 ppm, respectively. The carbon monox-

| Fuel | Calorific Value MJ/kg | Specific Gravity | Kinematic Viscosity @40°C cSt | Flash Point °C |
|---------|--------------------------|------------------|-------------------------------------|-------------------|
| ASTM | D240 | D4052 | D445 | D93 |
| Diesel | 42.891 | 0.831 | 2.73 | 79 |
| Si 0.25 | 43.478 | 0.8331 | 2.79 | 76 |
| Si 0.5 | 43.731 | 0.8352 | 2.82 | 71 |
| Si 0.75 | 43.789 | 0.8372 | 2.87 | 73 |

(a)



(b)

Figure 6: Physico-chemical properties of the tested fuels by authors in [38] and load carrying capacity of the fuels.

ide (CO) emissions were decreased by employing biodiesels with MgO and SiO_2 NPs, obtaining the maximum average reduction for SiO_2 nanoparticle with 25 ppm dosage (corresponding to a percentage of 10.4%). Incomplete combustion was obtained due to the shortage of air and reduced time allowed to complete the combustion. Also, adding oxygen-containing nano-particles to the biodiesel, the CO emissions were strongly reduced by providing additional oxygen to the air-fuel mixture. The emissions of carbon dioxide (CO_2) were increased by adding MgO and SiO_2 nano-particles, as well as the emissions of nitrogen oxides (NOx) were decreased; this reduction of NOx emissions is attributable to the enhanced combustion of enriched biodiesel due to the catalyst effect of NPs addition, which helps heat transfer in the combustion chamber. Therefore, the authors demonstrated that MgO and SiO_2 nanoparticles with 25 ppm dosage can be used as extra low-cost additives for biodiesel to decrease pollutant emissions in diesel engines. In addition, the researchers demonstrate that the addition of cerium oxide nano-particles increase the viscosity and the flash point of biodiesel; furthermore, they demonstrated that the emissions of hydrocarbon and NOx significantly dropped with the addition of the aforementioned nano-particles to fuel [37]; the following table 2 resumes the results obtained by the authors in their research works.

In [38], the authors tested in a twin-cylinder diesel engine the effects on combustion performances and emissions of a fuel enriched with Si nano-additive. This additive was mixed according to different weight concentrations with diesel fuel for preparing the fuel samples. The tests were performed at a constant speed (1200 rpm) and

by changing the load conditions. Among the different considered fuel samples, those enriched with 0.5 wt% Si nano-additive showed a higher load carrying capacity. Also, the torque rose of 5.91% and NOx emission dropped by 27.3% compared to diesel fuel at 1200 rpm and 100% load condition. According to the authors, the enhancements of the engine performances and pollutant emissions for the tested fuels are ascribable to the variations of both heat release rate and combustion timing due to the nano-additives addition. Furthermore, the tested fuels, with three different concentrations of Si nano-particles, were further studied by the authors to determine the modifications of the physical and chemical parameters due to the *nano-additives* addition. The variation in the physical and chemical parameters of the tested fuels is shown in Figure 6a [38].

By adding the nano-additives with different concentrations (*i.e.* 0.25 wt%, 0.5 wt%, and 0.75 wt%), slight increments of calorific value, specific gravity, and viscosity were demonstrated, as well as the flashpoint shown a descending trend for the first two samples, but it increased for higher nano-additives amount. Figure 6 shows the torque produced by the tested fuel samples depending on the added Si nano-additives; for Si 0.5 fuel, the maximum load-carrying capacity was obtained, producing 98.5 Nm torque in correspondence of 1200 rpm speed and 100% loading condition. Also, 96 Nm torque was obtained for Si 0.25 fuel, as well as, in the same working conditions, diesel with no-additives produces lower torque (93 Nm); for fuel enriched with Si nano-additives, the maximum heat release rate is obtained, thus resulting in higher load-carrying capacity. The experimental tests demonstrated that Si 0.5 fuel shown better performance compared to the

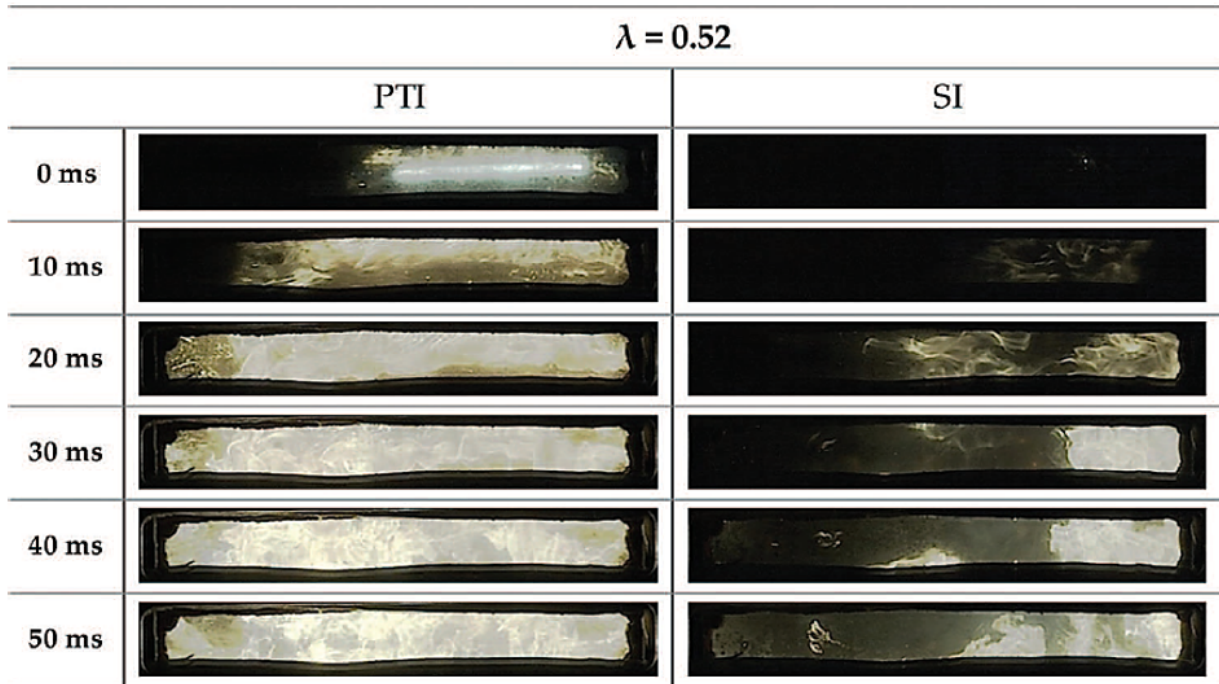


Figure 7: Frame sequences related to the combustion of air/ gasoline mixture with $\lambda = 0.52$; comparison between the ignition / combustion by MWCNTs/nEMs photo-thermal ignition (PTI) and spark ignition (SI) [39].

other fuel samples; the combustion tests carried out on enriched fuel samples indicated that *Si 0.5* fuel samples shown faster heat release rates and higher peak pressures in the combustion chamber. In addition, *Si 0.5* fuel shows a higher torque generation (+5.91%) and lower emission of *CO* (−28.57%) and *NOx* (−27.3%). Therefore, the authors concluded that *Si 0.5* fuel provides better combustion performance and emission characteristics than diesel.

The innovative volumetrically distributed ignition approach was discussed in depth by authors in [39] where the innovative photo-ignition method is proposed to control the starting of the auto-ignition process, by employing the photo-ignition properties of CNTs; specifically, we have already proposed in several research works the structure and related experimental results of a new light-induced ignition system adaptable to gaseous or liquid fuels, that leads to superior performances, in terms of combustion duration, ignition delay, pressure peak, combustion efficiency (for all the tested fuels: CH_4 , LPG, and H_2) [1, 2, 40, 41]. The following frame (Figure 7) shows high-speed images of a single combustion event in each case, initiated by the two ignition systems. Two series of pictures related to the combustion process with photo-thermal ignition (PTI), left column, and spark ignition system (SI), right column, are reported. As evident also from the first frame after the ignition, an instantaneous and volumetric ignition of the MWCNTs/nano-energetic particles takes place in the com-

busion chamber after the starting of the flash generation, with consequent ignition of the entire charge. Indeed, the combustion chamber is fully illuminated starting from the third frame. The light radiated by the burning process is visible along with the entire chamber until the completion of the combustion process. Such ignition modality could be explained with the high spatial dispersion of the nano-ignition agents within the combustion chamber, which can simultaneously ignite the charge combustion also far from the luminous source location.

Conversely, in case of ignition employing a spark plug, the combustion process shows an ignition phase that is longer and featured by a flame evident from the 5th to 6th frame. At first, just the air-fuel mixture near the spark-plug is involved in the combustion process, thus resulting in a volume with the high-intensity near the trigger point; afterward, the flame kernel propagates away from the spark-plug zone and burns the fuel in the combustion chamber. Since a rich air/gasoline mixture is used for the test depicted in Figure 6, high contrast images are obtained. If a lean air/fuel mixture is employed, a similar combustion process is obtained.

According to the authors, the benefits deriving from this typology of ignition system are ascribable to the spatially distributed ignition of the photo-thermal ignition, with a consequent faster and more complete consumption of the charge in the test vessel. Higher peak pressures and

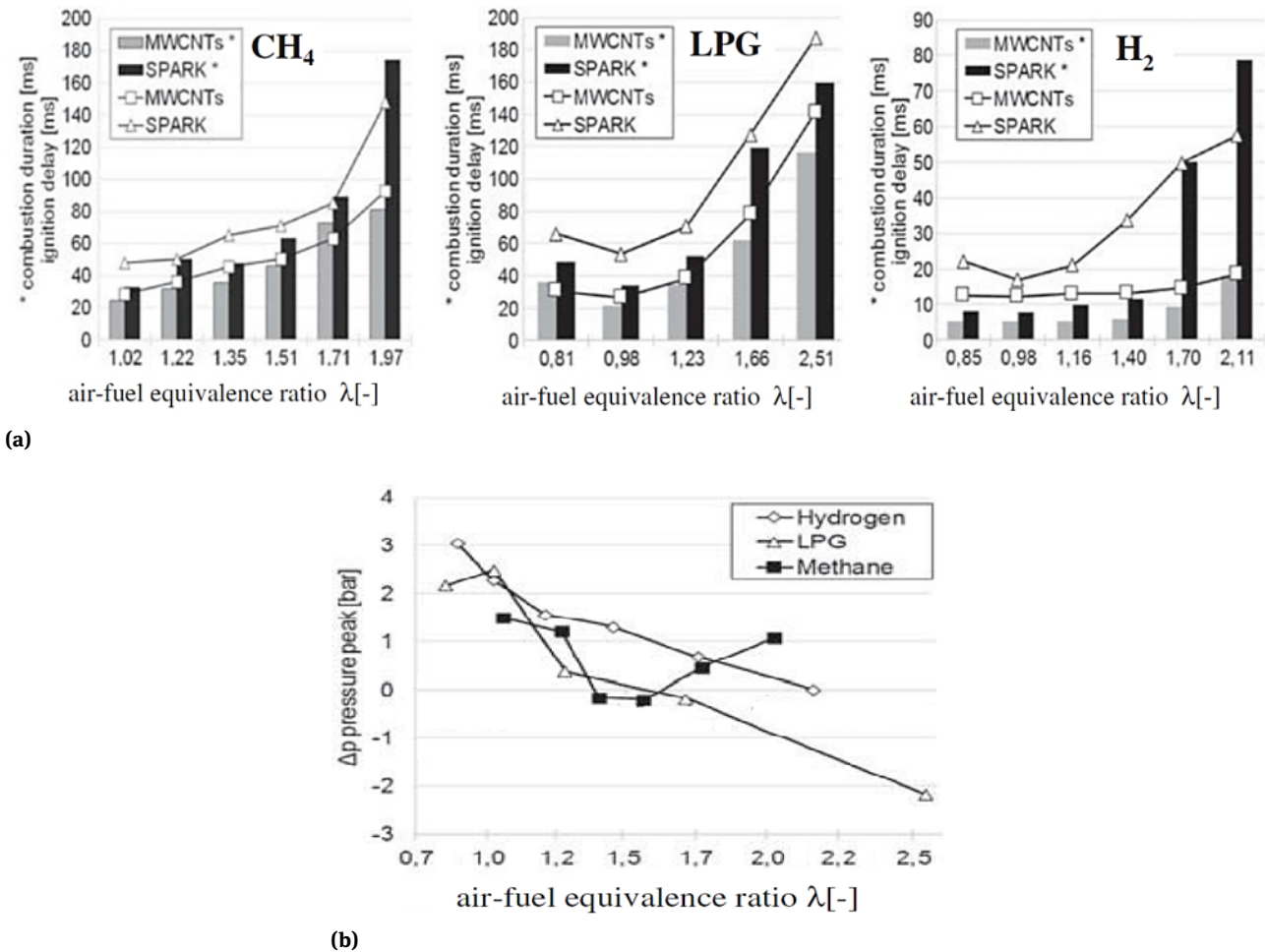


Figure 8: Histograms related to the comparison between combustion duration and ignition delay deriving by the use of nano-particles or spark-plug (a) and graph related to pressure peak obtained with the two ignition system (b) for all the tested fuels [1].

shorter rise periods are achieved by using the PTI system, thanks to numerous ignition nuclei that burn almost simultaneously, which results in a volumetric and distributed combustion in the combustion chamber. This is drastically different than the flame front propagation observed with the spark ignition.

The results of the tested gaseous fuels, in terms of ignition delay, combustion duration and pressure peak obtained by using nano-particles or spark-plug, are highlighted in the following graphs and table extrapolated from previous work performed by us, reported here for clarity [1, 2].

Besides to the results related to the combustion performances of fuel enriched with CNT nano-particles, the authors in [39] provided some consideration about the method to use for the introducing of the nano-particles within the combustion chamber; they highlight several ways to obtain this aim, for example, either by powder injection into the intake port or through mixing it with the

fuel and, also a system of fiber optic cables and flash lamp could be used to direct the flash energy into the combustion chamber. On the other hand, the researchers in their work, discuss about the main issue, of the proposed innovative method, related to possible environmental impacts of nano-metric carbonaceous materials in the combustion process, given potential generation, inside the engine, of condensation nuclei, with further formation of particulate and other nanostructured materials escaping the combustion process, which can end in the atmosphere. The effects of the combustion products on human health and environment cannot be simply inferred by the researchers in the current stage. In this context, shorter combustion and precise control of ignition time can enable more flexibility to modify the engine internal structure, and related operative parameters, with direct consequences on pollutant emissions; particularly, the thin particle and particulate emissions issue is of particular concern in the last years. However, several filtering systems are equipping many direct

injection engines already available on the market, like the particulate filters used in diesel engines to reduce particulate emissions [39–41].

5 Photo-induced fuels combustion by means of laser in automotive/propulsion fields

The use of laser for triggering fuel combustion inside the engine cylinder, without the use of photo-ignitable nanoparticles, is investigated by different researchers and automotive companies. Such ignition systems employ laser pulses with time duration of few nanoseconds, collimated through suitable optical groups in the engine cylinders, for igniting air-fuel mixture as discussed below [3–14]. Moreover, with the recent advances of laser technologies, the main parameters to act on to control the fuel ignition are the laser pulse energy, wavelength, pulse duration, besides optical techniques and selection methods for distributing (in space or time) the laser energy in either single or multiple ignition events. In this context, a very active research topic is the dynamic selection and optimization of the aforementioned parameters for obtaining a more cleaner and efficient combustion in any operating condition of the engine [3–8, 42]. Figure 9 shows a low-power laser ignition conceptual design with the laser ignition system focused on a metal target. In this conceptual design, by using a plate coated with SWCNTs as the laser's target material, a low-energy ignition system can be obtained [42].

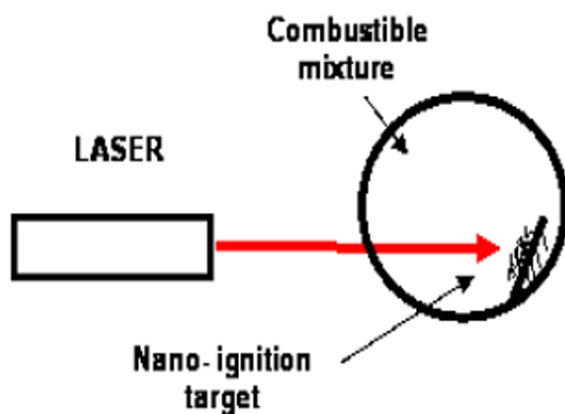


Figure 9: Laser ignition system using a target coated with SWCNTs [42].

The original reasons for using laser ignition as an alternative to the conventional ignition systems were to increase the efficiency of fuel combustion respect to the conventional engines and to reduce the pollutant emissions; moreover, a further factor accelerating the interest on the use of laser ignition was the growing trend to build lean-mixture engines [3, 42].

The use of the laser to photo-trigger the fuels' combustion is investigated by different research works [4–12]; for example, laser ignition for aerospace propulsion is analyzed in [4]. The research of newer and more advanced ignition techniques is an ever-present topic in the automotive field, as well as the continuous development of solutions for reducing the pollutants levels (*i.e.* CH_x , NO_x , and SO_2), in order to comply with increasingly stringent pollution regulations. Many aviation gas turbine manufacturers are interested to increase combustion efficiency in engines, all the while reducing the emission of harmful pollutants. Furthermore, the advanced ignition techniques will allow taking full advantage of new propulsion technologies (as scramjet propulsion) which are very desirable for the new generation of aircraft and spacecraft. In this scenario, the use of spark ignition methods is a heavily limiting factor, thus pushing researchers to seek innovative ignition techniques [4].

For the authors in [5], the laser ignition can solve several issues, besides to offer numerous benefits compared to conventional ignition methods (as spark plugs), such as: to collimate (laser) the energy in any desired location of combustion chamber, no quenching of the combustion flame kernel, to distribute the energy simultaneously to multiple locations, and carefully control the ignition time; thanks to these benefits, the engine efficiency could be enhanced and a reliable operation with high air-fuel ratio could be obtained, enabling the reduction of fuel consumption and abatement of pollutants emissions. The laser ignition method paves the way towards new solutions to addressing issues regarding environmental impact related to the continuous exploitation of fossil fuels used for supplying internal combustion engines employed in all fields of human activities. The technological advances can also impact on the diffusion of electrification to powered transport, due to the introduction of innovative ignition systems to hybrid engines, and to the efficient combustion of advanced fuels. In Ref. [5], the researchers investigated the possibility to deliver a laser beam from the laser source to the engine; this activity is very attractive, but the issues associated with the laser used in the experiments (in principal large size and heavyweight, or low output efficiency) and the position where laser should be located in a car engine require still a solution. Therefore, to use laser (but

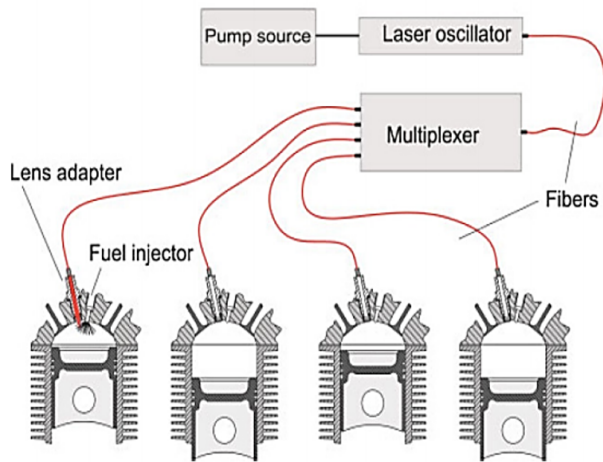


Figure 10: Schematic representation of laser ignition system, where the laser beam is distributed by optical fibers to multiple engine cylinders. The laser source includes a pump source and oscillator, whereas an optical multiplexer is needed for routing the light beam towards the different engine cylinders [6].

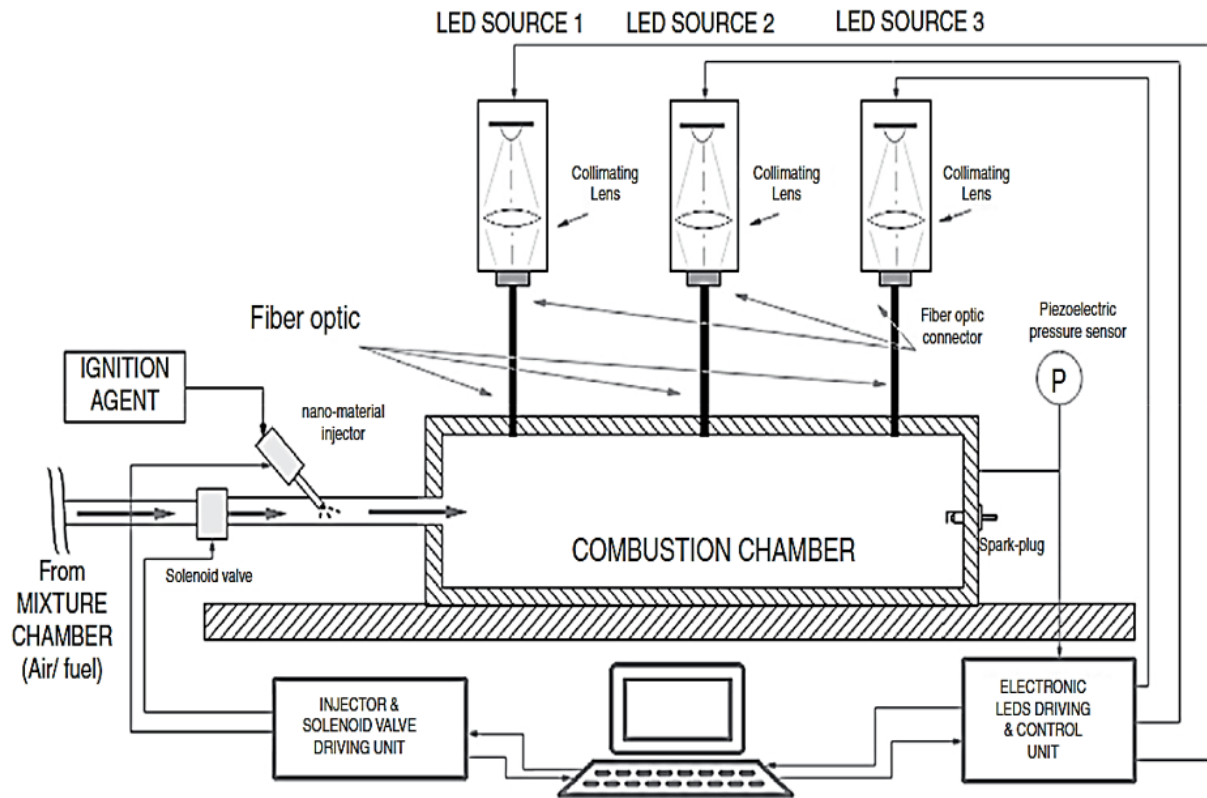
also LED sources) inside a car engine (coupling the produced light with optic fibers), an accurate design of light sources should be carried out, in order to make them of small dimensions, with a high-peak power, and able to withstand the harsh conditions that occur in an car engine (as high temperature, high humidity, vibrations, etc.). For instance, different researchers and companies agree that for multi-point ignition systems, featured by different triggering points, a viable solution is that depicted in Figure 10, where a single laser source is connected by a multiple fiber optic with the engine cylinders through an optical multiplexer [6]. This solution is very beneficial since just a single laser source is necessary, which could be positioned far from the engine, where high temperature and vibrations could damage it; nevertheless, the design of an efficient fiber optic delivering system is crucial. The laser sources commonly used to trigger the combustion are featured by ~1-10 MW peak power; such high power values impose additional requirements to the delivering optical fibers, as well as for the spark creation, a high beam quality (spatial-quality) to the fiber exit is needed, in order to refocus the light beam for creating the spark. According to several researchers, the use of conventional step-index fibers makes the design of the fiber-based delivering system intractable or very challenging. In multi-cylinder engines, an optical multiplexer is needed for distributing the laser pulses produced by the single source to the multiple fibers connected to the engine's cylinders [6].

The schematic diagram reported in Figure 10 suggests the use of optical fibers as also illustrated by our schematic diagram related to the LED-based solution (Figure 11a),

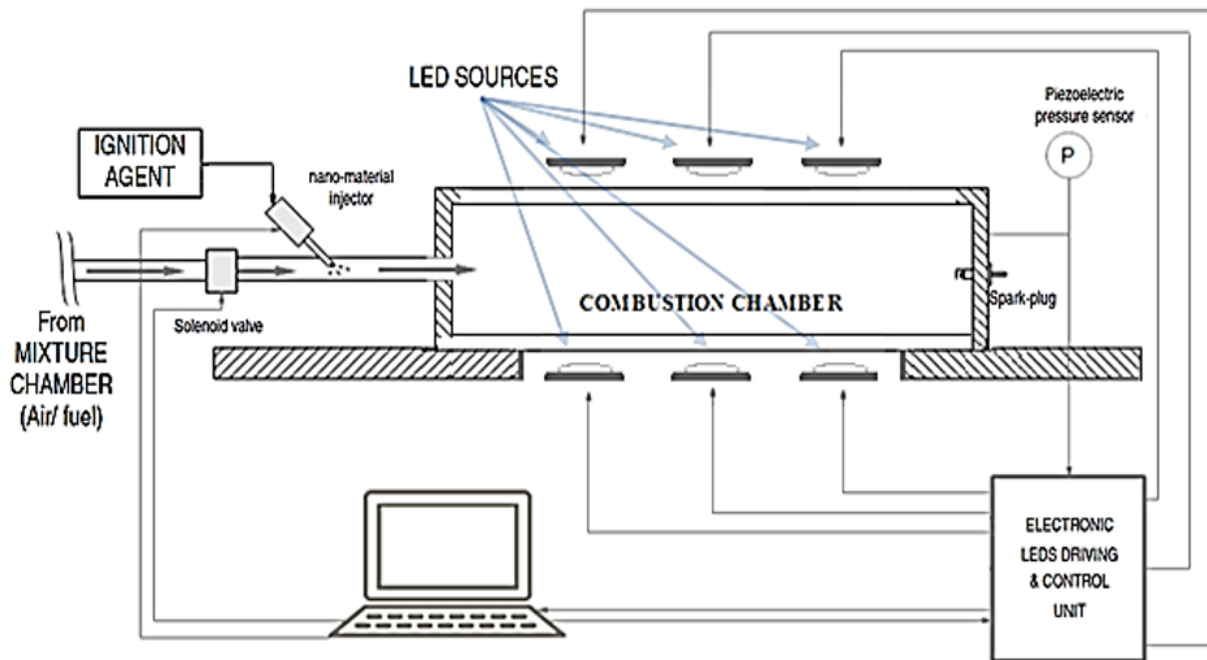
where, however, the fuel combustion is obtained by photo-igniting the CNTs/nano-particles dispersed into the air-fuel mixture; obviously, in the experimental setup of Figure 10, in place of the combustion chamber shown in Figures 11a (reported also in our published research work [2]), the optical fibers are directly connected to the engine cylinders. In alternative, the LEDs can be arranged directly coupling the light sources with the combustion chamber by quartz windows, as shown in Figure 11b.

The light emitted by LEDs can reach a larger area of the combustion chamber (or engine cylinder), so allowing to ignite simultaneously a greater number of nano-particles inserted into the cylinder, in order to obtain combustion parameters similar or better to those obtained by using the Xenon lamp [1, 2, 39–41]; moreover, the LED sources enable the generation of light pulses with time durations compatible with the frequency range typical of automotive applications. As example, by supposing, in the worst case (high-speed motor), that the motor operates at 4000 rpm (≈ 66 rps) and by considering that a four-stroke motor performs an explosion every two revolutions, then, the ignition system has to perform 2000 ignitions/minute (≈ 33 ignitions/s); in this case, the LED source has to operate at 33 Hz (with a period equal to about $T = 30$ ms). Hence, considering a time duration of light pulse for the CNTs ignition equal to 10ms, the duty-cycle (D) of the signal that controls the turning on/off of the LED source is given by: $D = T_{ON}/T = 10\text{ ms}/30\text{ ms} = 0.33 = 33\%$. Therefore, the time duration of light pulse for triggering the CNTs ignition has to be reduced in order to make possible the use of LEDs sources in the automotive/propulsion field. However, further improvements of the optical sections used to focus and collimate the light generated by LED source are required, for ensuring a higher luminous power emitted by the source. Indeed, the LED source employed in our work featured high optical losses (nearly the 70% of the luminous power generated by the “naked” LED), because of the relatively high F-Number of the used optical system, namely the ratio between lens' focal length and diameter (because of the small dimensions of used lenses) [24]. Therefore, a trade-off is needed between the high energy densities, obtained by collimating the emitted light as much as possible and the luminous intensity leakages [24].

On the other hand, as already discussed, also laser is a good candidate to be employed in the automotive field for triggering the fuel combustion. As example, the concept for a laser spark plug was described in [7–14]; the solution for “non-central ignition source” with one ignition laser on each cylinder of an engine and a pump source located apart is suggested by many researchers.



(a)



(b)

Figure 11: Experimental setup used to carry out the combustion tests on different air-fuel mixtures that employs optical fibers to convey the light emitted by LED sources into the combustion chamber (or into the cylinder as reported in Figure 10 related to the use of lasers) (a); view of a similar experimental setup where LEDs sources are directly coupled with combustion chamber by quartz windows.

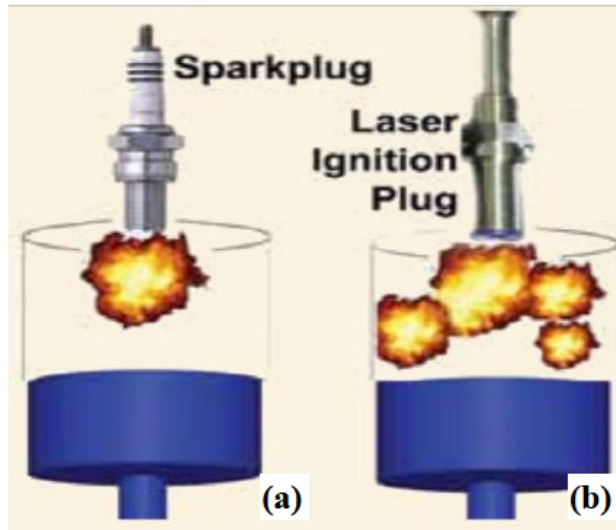


Figure 12: The spark plug ignites the fuel at the top (a), whereas the laser ignition plug simultaneously lights the fuel in multiple locations (b).

A fully functional laser ignition system was built by Takunori Taira's research group at *Japan's National Institute of Natural Sciences*, working with *Toyota Motors*, *Nippon Sokem Inc.*, and *Denso Corporation*. They demonstrated the world's first gasoline engine car with a micro-lasers ignition system in 2013; the laser ignition plug splits the laser beam by integrated optic lens, so that it will simultaneously ignite fuel in different locations of the compressed gas. In contrast, a spark plug has only one point of ignition as shown in Figure 12, which reports a comparison between the two different ignition systems [8, 9].

The laser ignition will allow the automotive companies to improve the firing timing of the engine, switch to a leaner air-gas mixture, and also increase the internal pressure in the engine cylinders. For the researchers, this ignition system will allow to make the combustion cleaner and further increase the engine efficiency; furthermore, the laser ignition system will reduce pollutant emissions released by the car in the atmosphere [9, 10]. For the authors, by realizing monolithic laser sources, will make the ignition system robust, and also economies of scale will be facilitated; also, the laser optical pumping has to be carried out in quasi-continuous wave, employing laser diodes with low peak power and optical fibers to convey the pumping beam towards the corresponding laser spark plug. A 3D illustration of an engine with mounted the laser ignition system is shown in Figure 13a and 13b [5, 7, 8].

A laser spark prototype (*Nd:YAG-Cr⁴⁺:YAG micro-laser*), shown in Figure 14a, with one-beam output, was realized at the *Institute for Molecular Science (IMS)* group,

Okazaki, Japan; several ignition tests were performed using this laser prototype, among which it was tested on a *gasoline direct injection* automobile engine (*IAZ-FSE, Toyota Motor Corp*). In carried out tests the *Nd:YAG-Cr⁴⁺:YAG micro-laser* was placed in the engine compartment and, by mirrors, the laser beam was collimated and then focused by means a *sapphire window (Al₂O₃ crystal)* in one of the engine cylinders, in the same location of the spark plug; the engine, with stoichiometric air-gasoline mixture, was ignited by means a 2.3mJ single laser pulse. Contamination or damage to the window was not observed after several hours of operation [5, 11]. By ceramic methods and in optically bonding of such all-polycrystalline have allowed advances in the developing of laser materials enabling composite structures to build laser prototypes which provide multiple-beam output (Figure 14b and 14c) [12, 13].

Therefore, as analyzed by different research works, the main advantage of laser ignition is the possibility to focus the light beam in any position, of the engine cylinder, enabling further engine optimizations. Through an accurate control of both ignition time (*e.g. using multi-pulse ignition method*) and ignition position (*e.g. using multi-point ignition method*), the engine can operate with lean air-fuel mixtures or at high pressures. Despite the simplicity and flexibility of the ignition methods above described, several technological and scientific challenges related to the design of optical fibers resistant to high temperature and vibrations have to be faced. Furthermore, the most attractive solution for laser ignition, especially for automobile and space applications, is to place the laser spark plug(s) directly on the engine cylinder, optically pumping it with a light source located far from the engine, to preserve this last from the harsh conditions present near the engine [43].

The development of compact lasers sources perfectly compatible with the engine as an alternative of the common spark-plug, and robust enough to operate in environments with vibrations and high temperature is a challenge. However, several models of laser spark-plugs are already present on the market; these models are all based on a laser medium constituted by a composite *Nd:YAG/Cr⁴⁺:YAG* structure (single crystal or polycrystalline), equipped with a monolithic oscillator. The *Nd:YAG/Cr⁴⁺:YAG* lasers are optically pumped by laser diodes, either fiber-coupled or in array configurations, which are arranged according to either longitudinally or laterally respect to the active medium. The *Vertical-Cavity Surface-Emitting Lasers (VCSELs)* represent the most promising pumping source, given the better stability of the output performances (*e.g. the emitting wavelength*) with the device's temperature [5, 12–14].

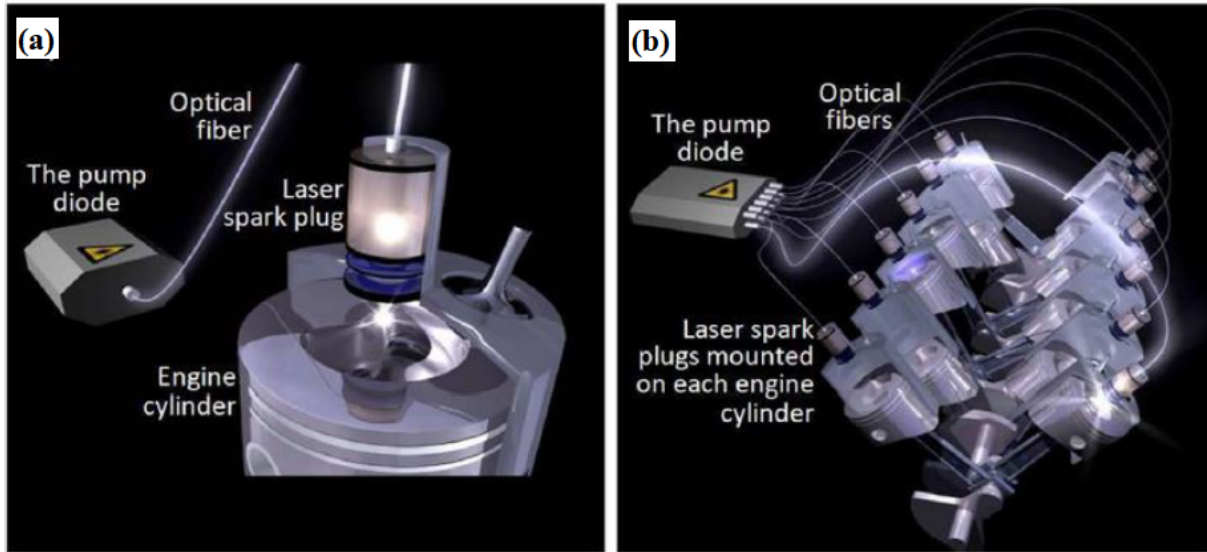


Figure 13: Computer illustration of an end-pumped by fiber-coupled diode lasers, passively Q-switched solid-state laser with pump diode positioned apart from the engine and the laser head mounted directly on the engine cylinder (a) [7] and on a 12-cylinder internal combustion engine (b) [8].

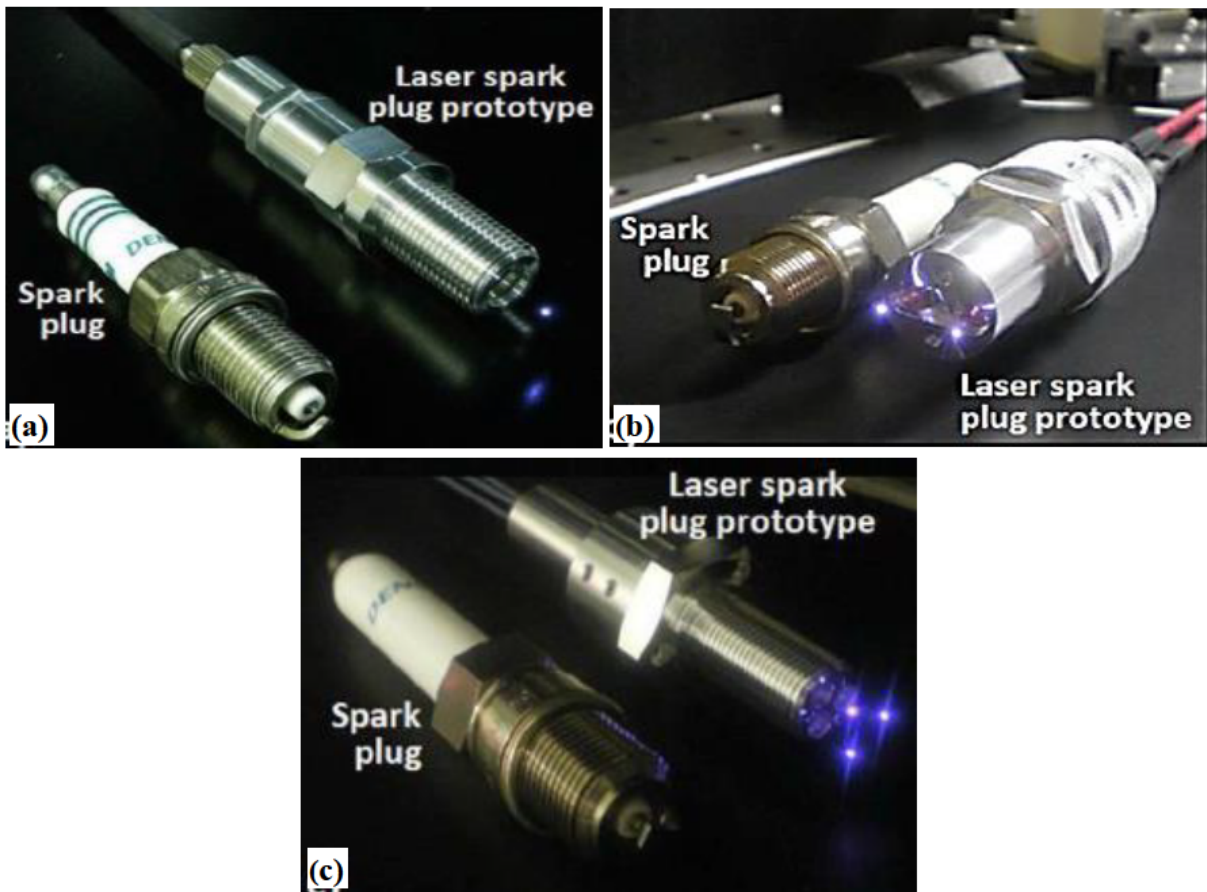


Figure 14: View of laser spark plug prototypes developed at IMS, Okazaki, Japan; single-beam solution with discrete elements (Nd:YAG, Cr4b:YAG single-crystals and resonator mirrors) (a), two-beam solution based on composite all-ceramics Nd:YAG/Cr4b:YAG in monolithic design (b) and three-beam solution (c) [11–13].

Besides the first prototype of the engine entirely propelled by laser-spark, developed by researchers of *IMS Okazaki, Japan*, in collaboration with the *Denso Company* cited above, also researchers in Romania (in collaboration with *National Institute for Laser, Plasma and Radiation Physics, Magurele* and *Renault Technologies Romaine*) successfully tested the laser spark-plugs on a car engine; Figure 15 shows the Renault engine where the air-fuel mixture is ignited by laser plugs.

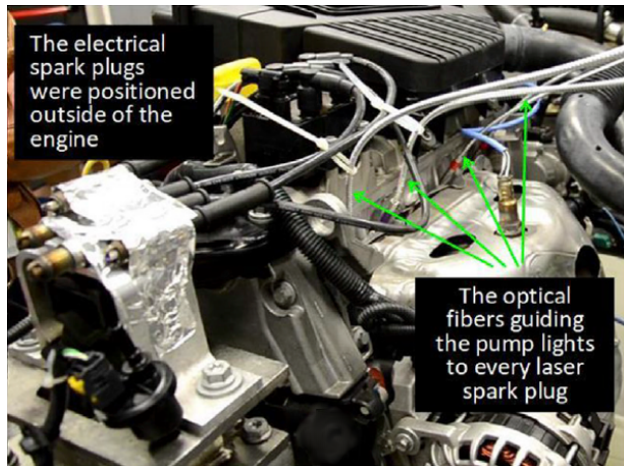


Figure 15: View of a Renault engine ignited by means of laser spark plugs during the carried out experimental test by researchers in [5, 13].

Furthermore, the stability measurements and exhaust emissions analysis were performed on a 4-cylinder test engine, demonstrating a significant improvement in engine stability by employing a laser ignition system, especially at low speed and moderate load; a reduction of HC and CO emissions were detected by using the laser ignition system but, in contrast, the NO_x emissions increased compared to the ignition through the classical spark-plugs [13].

6 Future developments and conclusions

Considering the discussion afore reported concerning the potentialities of laser-based ignition devices in the automotive field, also the LED sources offer similar advantages in terms of efficiency, robustness and driving simplicity compared to other light sources (e.g. Xe-lamp), as discussed in the previous paragraph. Therefore, these last represent a smart solution for triggering the fuel's combustion by means of the nano-particles photo-ignition. For au-

tomotive applications, the main limitation of LED sources encountered by us during the carried out experimental tests is the low power density mainly due to the high optical losses in the collimating and focusing sections, which limits the operating frequency of the ignition system to values not compatible with those of a car engine [24]. Many researchers and companies have investigated the use of laser sources for igniting the combustion of liquid or gaseous fuels in automotive engines and developed some laser-based implementations, such as the laser spark plug emitting one or more light beams; hence, the combined use of the NPs photo-ignition phenomenon and a laser-based ignition system can be considered, thus obtaining an ignition system for gaseous or spray of liquid fuel, enabling improvements of the combustion process inside the engine cylinder, even with energy savings respect to the classic ignition system. Therefore, by combining the two methods, *i.e.* the combustion triggered by laser-beam and nano-particles photo-ignition, with the aims of more uniform and complete combustion, a solution exploiting both the advantages provided by two systems is proposed in Figure 16. The new solution uses a multi-point laser source for igniting the nano-particles dispersed inside the air-fuel (gaseous or spray of liquid fuel) mixture, through two powder injectors placed on both sides of the cylinder. The two injectors/nozzles ensure a better distribution of nano-material inside the cylinder volume, and in conjunction with a multi-point laser, more homogenous combustion is obtained. The system could operate indifferently with both gaseous fuels or spray of liquid fuels, depending on the cylinder is equipped with a nozzle or an injector, respectively. A similar system could be employed also for igniting liquid fuels by the photo-ignition of the *Sea Urchin-Like Carbon Nanotube (SUCNT)/nEM* composite pellets as ignition agent, described in Ref. [19]; since this nano-material typology is waterproof, such ignition system could find application in the liquid-propellant rocket.

The employment of nano-particles' injectors for introducing the powder (e.g. CNT/ferrocene mixture or other nano-materials typology) inside the engine cylinder was already suggested by authors in the references [2, 39]; in these our previous works, we proposed different methods for introducing NPs in a combustion chamber, among which the use of the injectors, as cited in the previous section. Obviously, for the right engine operation, all supporting systems have to be synchronized, namely the air/fuel injection inside the cylinder, the nano-particles injection and finally the light beam emission by the laser have to occur in precise and scheduled instants; in particular, soon after the injection of the air/fuel mixture and nano-particles inside the cylinder, procedures that can be per-

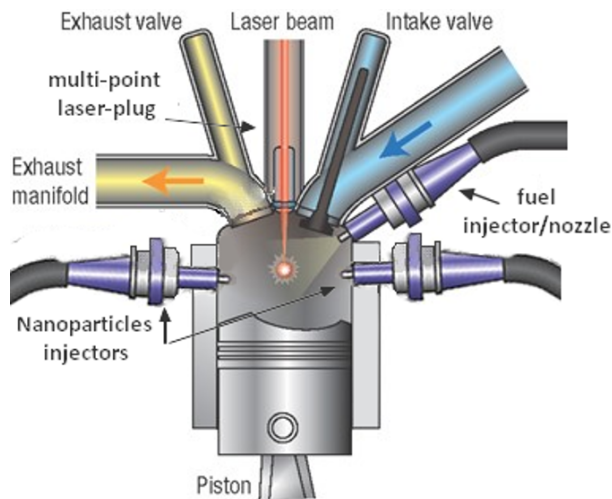


Figure 16: Image of an engine cylinder equipped with the proposed ignition system: the laser plug, with laser beam highlighted, is used to photo-ignite the nano-particles dispersed into the air-fuel mixture through two injectors/nozzles placed on both sides of the engine's cylinder.

formed simultaneously, the laser beam has to be activated for triggering the fuel combustion by means of the photo-ignited NPs. The adding of these last will allow to obtain homogeneous combustion in all the cylinder volume, contributing to have a lower NO_x emission than that measured in Ref. [14].

Alternatively to the laser-based solution (Figure 16), a new system employing LED sources could be developed, as extension of the experimental setup reported in Figure 11a, applied to the engine cylinder; similarly to laser-based solution, also in this case the LED sources could be placed remotely respect to the engine and coupled with it by suitable optical fibers.

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