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Multi-Walled Carbon Nanotubes (MWCNTs) bonded with Ferrocene particles as ignition agents for air-fuel mixtures

Antonio Ficarella [a], Antonio Paolo Carlucci [a], Bruce Chehroudi [b], Domenico Laforgia [a], Luciano Strafella [a,*]

[a] University of Salento, Department of Engineering for Innovation, Via per Monteroni, 73100 Lecce, Italy
[b] Department of Mechanical Engineering, Arkansas Tech University, Russellville, AR 72801, USA

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ABSTRACT

The potentials and characteristics of a new ignition system for air-fuel mixtures are discussed. This ignition method (referred to as photo-thermal ignition) is based on light exposure of Multi-Walled Carbon Nanotubes (MWCNTs), bonded with other nano-Structured Materials (nSMs), (collectively referred here as ‘‘nanoignition agent”), using a low-consumption camera flash. Here, Ferrocene, an organometallic compound, was used as the nSMs.

Results from, and benefits of, this new ignition method are compared with a conventional spark-plug-initiated ignition used in automotive engines.

The main objective of this research is to demonstrate ignition feasibility of mixtures of both gaseous and liquid fuels with air under high pressures using the photo-thermal ignition (PTI) phenomenon. Specifically, the ignition and subsequent combustion characteristics of gaseous air-fuel mixtures at different air-fuel ratios were investigated by means of light exposures of nano-ignition agents (nIAs) after they are mixed with air-fuel mixtures.

Analysis of the acquired data showed that for the range of air-fuel ratios tested, the photo-thermal ignition with a flash lamp resulted in a higher peak chamber pressure when compared to those obtained with a conventional spark ignition system. Heat release rate analysis showed that shorter ignition delays and total combustion durations for the Photo-thermal ignition are achieved. Comparative percent reduction of these values for photo-ignition ranges from 20% to 50% for LPG and methane, whereas values up to 70% were observed for the hydrogen. The positive impact of the photo-thermal ignition appears to be primarily at the ignition delay period of the combustion. With liquid fuels, photo-thermal ignition was capable to ignite mixtures as lean as a relative air-fuel ratio of 2.7 while the spark ignition was incapable to initiate combustion. Additionally, tests with the liquid gasoline injection highlighted that the combustion process with a higher ‘‘residence mixing time” exhibited higher peak pressures and shorter ignition delay times.

High-speed camera images were used to capture images of the light emission during the combustion process in visible range, allowing investigation of the ignition processes. In particular, the results showed that the photo-thermal ignition process of the air-fuel mixtures with nano-ignition agents led to a *spatially-distributed ignition* followed by a faster consumption of the air-fuel mixture with no evidence of any discernible flame front formation or propagation.

1. Introduction

The ignition system and control of the combustion process are at the heart of every combustion process in internal combustion engines. For years, researchers have been seeking alternatives to conventional combustion processes for high performance and low emissions of pollutants, in particular, nitrogen oxides (NO_x), carbon monoxide (CO) and particulate matter (PM). In diesel engines, the ignition is achieved through a compression process of non-premixed air-fuel mixture by the piston during the compression stroke. This so-called compression-ignition process is

Abbreviations: MWCNTs, Multi-Walled Carbon Nanotubes; SWCNTs, Single-Walled Carbon Nanotubes; CNTs, Carbon Nano-Tubes; nSMs, nano Structured Materials; nIAs, nano-Ignition Agents; PTI, Photo-Thermal Ignition; SI, Spark Ignition; HCCI, Homogeneously-Charged Compression-Ignition; NO_x, Nitric Oxides; CO, Carbon Monoxide; CO_2, Carbon Dioxide; Xe, Xenon; MIE, Minimum Ignition Energy; HRTEM, High-resolution transmission electron microscopy; TEM, Transmission Electron Microscope; Fe, Iron; Fc, Ferrocene; O.D. × I.D. × L., Outer Diameter × Inner Diameter × Length; CH_4, Methane; H_2, Hydrogen; LPG, Liquefied Petroleum Gas; HRR, Heat Release Rate; cumHRR, Cumulative Heat Release Rate; λ, Relative Air-Fuel ratio.

* Corresponding author.
E-mail address: luciano.strafella@unisalento.it (L. Strafella).

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highly sensitive to operating conditions such as ambient temperature and pressure, and is characterized by two different burning phases (premixed and mixing-controlled phases). On the other hand, in gasoline engines, the ignition of a premixed air-fuel mixture (at stoichiometric ratio for most engines) is obtained by an electric spark, generating a relatively slow-burning flame front at the spark gap location which propagates while burning the air-fuel mixture (Fig. 1).

An alternative technology is represented by the Homogeneously-Charged Compression-Ignition (HCCI) burning process. The HCCI is a form of alternative internal combustion engine, or combustion mode, in which a lean-premixed homogeneous mixture of fuel and oxidizer ignites (or auto-ignites) when the mixture temperature during the compression phase of the engine operation increases. In this manner, the combustion process involves the entire mixture trapped inside the cylinder (Fig. 1, the first image from the right). In both HCCI and conventional spark ignition engines, the fuel and air are mixed before the start of the ignition process. This homogeneous mixture of fuel and air (especially at lean mixture ratio for the HCCI case) substantially reduces the soot emission as compared to that seen in diesel engines. The ignition (or auto-ignition) process in HCCI engines exhibits multiple ignition points distributed throughout the combustion chamber. This, when combined with combustion of the lean premixed air-fuel mixtures, keeps burn-gas temperatures at lower values, which consequently prevents formation of nitrogen oxides (NO_x) and delivers a remarkable reduction in fuel consumption [1,2].

However, the critical requirement for proper operation of the HCCI engines is a precise control of the auto-ignition process [3,4], namely, the control of the time at which auto-ignition of the premixed gaseous air-fuel mixture inside the combustion chamber takes place. Using a variety of complex control systems, based on parameters influencing the beginning of the auto-ignition process, it is possible to efficiently operate a HCCI engine. However, these controlling systems are still extremely complex, expensive, and onerous [1]. This stems from the fact that the onset of the auto-ignition in premixed air-fuel mixtures is very sensitive to engine operating and design parameters.

In order to address this ignition control problem for the HCCI combustion, an innovative light-activated volumetrically-distributed ignition approach has been proposed by Chehroudi [5] to directly control the beginning of the auto-ignition process. This approach is based on the observation that carbon nanotubes, when exposed to a low-consumption short-duration light sources, ignite collectively and burn [5]. Therefore, they could act as auto-ignition nuclei when mixed with a homogenous fuel-oxidizer mixture and exposed to pulsed light sources, such as an ordinary camera flash (Fig. 2).

Fig. 3 shows carbon nanotube samples before, during and after the ignition by an ordinary camera flash. The use of the photo-thermal ignition system has the following advantages compared to the other ignition systems:

- The ignition is achieved remotely and distributed spatially at a large number of locations.
- The volume within which ignition takes place can be adjusted to achieve both localized and variable-size volumetrically-distributed ignition.

A carbon nanotube (CNT) is a hollow nanostructure like a hollow cage consisting of essentially a graphitic plane rolled into a thin tube, both ends of which can be closed by a fullerene-type dome structure. The existence of CNTs was originally discovered by S. Iijima [6] and have been the subject of intense study since their discovery (Fig. 4). The material exhibits various interesting mechanical and electrical properties. There are two forms of carbon nanotubes, namely Single Walled Nanotubes (SWCNT) consisting of a single layer of graphene rolled into a tube whose diameter depends on the chirality of the nanotube, and Multi Walled Nanotubes (MWCNTs) that can appear in a coaxial assembly of SWCNT similar a coaxial cable, or as single sheet of graphite rolled into the shape of a scroll (Fig. 4 and Fig. 5).

Photo-thermal ignition (PTI) has been observed in SWCNTs [7], MWCNTs [8], graphene oxide [9], silicon nanowires [10], polyanaline nanofibers [9], and certain types of metal-doped activated carbon [8].

It has been reported by P. M. Ajayan et al. [7] that carbon nanotubes released a large photoacoustic effect and ignited when subjected to a flash of light due to efficient absorption of the light energy (Fig. 6). According to Ref. [7], it seems that the phenomenon is predominantly present in SWCNT's and that the temperature of the process can reach between 1500 and 2000 °C at the very localized points of ignition. The researches have also determined that activated carbon containing a metal such as palladium also possesses the property of releasing a photoacoustic effect when subjected to a flash of light.

The authors in Ref. [11] demonstrated that the photoacoustic and ignition effects are attributed to rapid increase in temperature resulting from absorption of the light flash by CNTs. Here, the nano-Ignition Agent (nIA) samples consisted of iron (Fe) nanoparticles mixed with fluffy SWCNTs. They also showed that the higher the content of the nanoparticles, the easier the ignition of the SWCNTs took place (i.e., lower ignition energy needed). For more

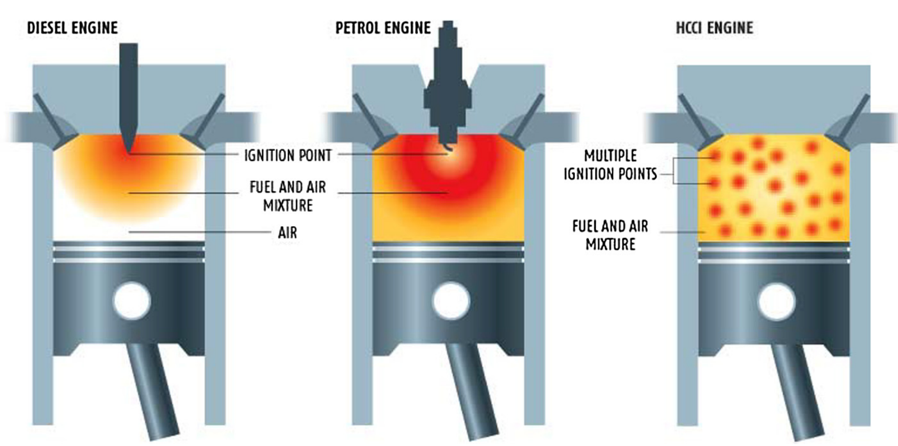

Fig. 1. Ignition and combustion process in several internal combustion engines.

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