Experimental Analysis of the Influence of Inert Nano-additives upon Combustion of Diesel Sprays

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Abstract
Recent experimental studies report that addition of nanoparticles (typically metal oxides nanopowders, such as Al₂O₃) can somehow modify the ignition mechanism of liquid fuels, probably influencing and accelerating the thermal exchange process between the fuel droplets and the surrounding air. In this paper it has been experimentally analysed a stationary Diesel spray, produced by a gas assisted atomizer, preliminarily comparing the behaviour of the flame generated using the unseeded fuel with that one of the same fuel additivated with Al₂O₃ nanoparticles. Results obtained through light emission analysis are encouraging, in the sense that the presence of a small nano-additive quantity (0.1% in volume) seems to produce effects similar to a shift towards higher flame ventilation, with a possible positive consequence upon combustion stability and efficiency.

Keywords
Nano-Additives, Diesel Spray, Combustion

1. Introduction
Nanostructured materials represent nowadays a wide and probably still largely unexplored field of potential applications[1]. In fact, this is a research topic in high and rapid development, both at a basic level and under the point of view of possible practical applications, leaving large space for a thorough scientific analysis, which requires with no doubt long time for ultimate conclusions.

The potential application fields of nanoparticles are very wide and, probably, not yet fully understood: from energetics (sensors, propulsion, reduction of environmental impact) to chemistry (catalysis, additives) to medicine (diagnostics) and of course to material science. Also the problem of nanoparticles impact on human health is a rather unexplored field. Among the possible applications, recent experimental studies[2] report that addition of nanoparticles (typically metal oxides nanopowders, such as Al₂O₃) can somehow modify the ignition mechanism of liquid fuels, probably influencing and accelerating the thermal exchange process between the fuel droplets and the surrounding air. In fact, the added nanoparticles can be small enough to approach molecular dimensions, modifying the physical properties of the liquid fuel (such as thermal conductivity, mass diffusivity and radiative heat transfer) and at the same time increasing the surface-area-to-volume ratio of the fuel droplets allowing more fuel to be in contact with the oxidant.

These studies are focussed on the analysis of the ignition probability of additivated fuel single droplets impinging on a hot plate and it has been observed that ignition temperature of fuel mixtures containing nanoparticles is lower than that of pure Diesel fuel. In fact, ignition delay and ignition temperature are critical parameters to characterize the performance of a Diesel fuel, influencing both emission levels and efficiency of the combustion process. Moreover, it has been observed[3, 4] that the use of nanoparticles in rocket propulsion can enhance the engine performance under the point of view of specific thrust.

Anyway, no data have been yet reported about the possible influence of nanoparticles addition upon the combustion features of a Diesel spray. Therefore, in this paper it has been experimentally analysed a stationary Diesel spray, produced by a gas assisted atomiser, preliminarily comparing the behaviour of the flame generated using the unseeded fuel with that one of the same fuel seeded with Al₂O₃ nanoparticles.

2. Experimental Set-up
As previously outlined, the core of the apparatus consists of a gas assisted atomiser consisting of a capillary tube (0.3 mm inner diameter, 0.8 mm outer diameter) that lies in an opening of 1 mm diameter at the spray top, thus creating an annular gap. The liquid fuel flows under the action of a syringe pump (New Era Pump Systems Inc., Model NE-1000) inside the capillary at a flow rate of 1 ml/min. The dispersion gas (air in this application) flows inside the annular gap. The capillary ends a little downstream the opening, giving rise to an atmospheric spray flame ignited by a premixed
methylene-air flame which is concentrically arranged around the nozzle exit. This sustaining flame was kept just slightly rich, thus originating an overventilated cone in the presence of the oxidant. The gas flow rates are measured and controlled by thermal mass flow meters (Bronkhorst High Tech, The Netherlands). The apparatus is designed in order to achieve, through the longitudinal displacement of the dispersion gas injector, a variation of the outflow area, from zero to the maximum value. The combustion process has been confined inside a cylindrical quartz chamber (200 mm diameter), allowing full optical access, and the burned gases are conveyed in a hood connected with a sucking pump. The hood is equipped with a fibreglass filter (Whatman GF/A) placed rather far away from the flame tip, thus trapping the nanoparticles without being affected by hot gases.

A schematic view of the whole apparatus is reported in Fig. 1.

An easy way to comply with the paper

The Al$_2$O$_3$ nanoparticles used are produced by Nanostructured and Amorphous Materials Inc. (nominal average diameter=10 nm) with 99% certified purity. To obtain the alumina added fuel, the nanoparticles have been weighed and subsequently mixed in the fuel with different sonication cycles, ensuring the highest dispersion degree. Al$_2$O$_3$ has been selected because it can be considered as inert with respect to the combustion reaction, putting into evidence only a possible physical interaction with the various phenomena involved in spray combustion. Moreover, Al$_2$O$_3$ nanoparticles are rather easily available at a relative low cost, taking into account also the very low quantity of nanoparticles dispersed in the liquid fuel. In fact, for the preliminary analysis described in this paper, a volumetric percentage of 0.1% of nanopowders dispersed in the liquid fuel has been used. The percentage of the nanoparticles dispersed in the fuel has been selected on the basis of the results reported in[2] as the minimum value to obtain noticeable influence upon the ignition probability of the Diesel fuel. Therefore, this value has been kept fixed during the experimental measurements.

The fluid dynamic behaviour of the atomiser in isothermal conditions has been investigated through Phase Doppler Anemometry (PDA).

The preliminary comparison of the flame spray behaviour has been performed by emission spectroscopy and burned gases sampling and composition analysis. As for spectroscopy, it has been used a Tracor Northern apparatus equipped with a low resolution spectrograph. The radiation was collected by a quartz fibre through a yellow band-pass filter (597±30 nm); in fact, this spectral region is the more interesting under the point of view of unburned species formation. These lead to soot formation and then to black body emission. The flame region optically explored was roughly corresponding to the upper third of the flame plume. Burned gases have been sampled in the exhaust hood and the composition (NO$_x$, CO, SO$_x$, O$_2$, CO$_2$, excess air) has been characterised by an electrochemical analyser (Eurotron Greenline mod. MK2).

### 3. Results and Discussion

The experimental analysis has been performed upon the stationary spray, operated at atmospheric pressure.

In order to investigate the dimensional distribution of the generated droplets as a function of dispersion gas flow rate and gas to liquid mass ratio, the behaviour of the spray jet has been initially characterised in isothermal (cold) conditions, both through visualizations and PDA (Phase Doppler Anemometry).

Figure 2 summarizes the most representative obtained results. Particularly, Fig. 2A shows the comparison of the counter mean diameter (CMD) for the water spray and the n-hexane spray at 5 mm from the burner exit by varying the oxidant flow. For flows of oxidant higher than 2 l/min the size of the droplet is almost constant, particularly for n-hexane, which behaviour can be considered representative of hydrocarbon fuel. N-hexane fuel produces smaller droplets than water (about 11 μm against 19 μm). The radial profile of CMD was also investigated. As an example Fig. 2B shows the CMD radial profile for the water spray at 50 mm from the exit nozzle. The diameter of the droplet is almost constant with a value of about 13 μm.

It can be concluded that the “cold” spray is formed by droplets of about 15-20 μm average size, with operating
conditions almost constant inside a wide range of atomising air flow rate.

After the preliminary characterization of the spray behaviour, a qualitative imaging of the generated flame has been performed varying the operating conditions (i.e. mainly the air flow rate). Fig. 3 reports images of the spray flame obtained burning the pure fuel at a fixed flow rate (input thermal power of the spray flame=700 W) varying the atomising air flow rate. It can be observed that a decrease of the air flow rate induces a progressive formation of intense yellow coloured combustion regions due to higher particulate formation from unburned species.

![Figure 3. Images of the spray flame as a function of atomising air flow rate](image)

Temperature measurements along a radial profile using a B-type thermocouple (200 µm hot junction dimension) have been carried out to analyse the thermal behaviour of the premixed sustaining flame. Fig. 4 reports the results obtained corrected for the radiative losses, as reported in[11].

The profile at lower height (blue, z=0mm) corresponds to a minimum distance (about 1 mm) from the burner surface, which was the lowest accessible by the thermocouple arm. The profile has a hollow shape, owing to the receptacle of the spray nozzle, placed in the middle, then in the correspondence of the bottom part of the spray cone (r/R = 0.8-1). Moving upwards the temperature profiles tend to close, reaching at the centre about 900°C just at 3 mm height (pale blue). Here therefore, is where the nebulized spray is ignited (compare Fig. 3).

![Figure 4. Radial temperature profiles of the premixed flame](image)

Fig. 5 reports the comparison of the flame light emission (obtained as previously described) in the case of pure fuel and alumina loaded fuel, as a function of the atomising air flow rate. For this measurement, and in general for all measurements of this kind, an integration time of 18 s was set, thus intrinsically averaging short term fluctuations of the luminosity. It can be clearly observed an effect due to nanoparticles presence, giving rise to a general decrease of emission intensity from the flame, with a higher influence (up to 50% of intensity decrease) at lower values of air flow rate, that is just in the more critical flame conditions under the ventilation and nebulisation point of view. At higher values of air flow rate, the influence almost disappears and the curves tend to coincide. This, of course, does not mean that the effect of nanoparticles ceases, but simply that the effect is no longer detectable with this optical technique.

It is important to stress that the result of Fig. 5 is purely qualitative and strongly dependent on the particular flame structure under investigation. For instance, just a little change in the nozzle arrangement could largely alter the spray features and consequently the flame shape and luminosity in its absolute values, especially at the tip. The
only meaningful point here is the relative position of the two curves: the one laying below is expected to be originating from the flame exhibiting better combustion, as already observed in [12, 13].

Figure 5. Comparison of flame emission (band-pass filter at 597±30 nm)

However, to support the results of Fig. 5, two couples of points (1.95 and 2.2 Nl/min air) were tested with sets of 20 measurements each. All measurements were then averaged over the full set resulting in four experimental points covering a rather long measuring time. The luminosity of the seeded flame resulted steadily below the one of the pure fuel.

In order to confirm the possible positive influence of nanoparticles presence upon the combustion process, burned gases have been sampled and analysed. In this case, CO emission emerged as the more significant result (NOx formation being almost negligible and indistinguishable in the two cases). Fig. 6 summarizes the measurements obtained as a function of the atomising air flow rate: the presence of nanopowders in the fuel contributes to lower up to 7% the CO emission with respect to the pure fuel flame, confirming at least under a macroscopic point of view the improvement of combustion features due to nanoparticles addition.

Figure 6. Comparison of CO emission in the burned gases

4. Conclusions

The preliminary work performed suggests that the addition of nanoparticles to Diesel fuel (also at low concentration, i.e. 0.1% vol) can improve the combustion features of the spray flame, giving rise to lower CO emission levels and simulating a sort of higher-ventilation of the flame with respect to the unseeded spray, at identical air feeding conditions. Future experimental work is foreseen in order to deepen the results emerged till now, especially for sensitivity analysis of the spray flame to nanoparticles concentration in the fuel, typology and characteristic dimension of nanoadditives used, as a function of the operating conditions of the experimental set-up. Moreover, a theoretical study has to be performed in order to understand the influence of nanoparticles addition upon the combustion process, reaching a model of the involved phenomena.

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