INTRODUCTION

Experimental difficulties in following the soot formation and oxidation processes in the environment of diesel engines are recognised in the high values of the in-chamber temperature and pressure and the presence of extremely reactive intermediate species. At present, optical techniques have overwhelmed lacks typical of both local in-cylinder and total-cylinder samplings, which allow a high temporal resolution but give no insight into the instantaneous spatial distribution of the soot concentration [1-3].

From the point of view of modelling, complexity of the phenomenon has led a schematisation of the process to within various levels of approximation. Kennedy [4] distinguishes three main categories of models for soot formation and oxidation in combustion systems: purely empirical correlations, semi-empirical approaches solving rate equations calibrated against experimental data, and detailed models that predict the concentrations of all the important species in a flame from fuel to poly-aromatic hydrocarbons to soot.

Between empirical correlations, the ones by Kahn et al. [5] and Metha and Das [6], specifically conceived for application to diesel engines, can be considered of interest only due to the advantages in economy of calculations with respect to more detailed approaches. Kahn et al. assume that the rate of soot formation is entirely controlled by the soot inception rate, which is taken as a function of pressure, temperature and equivalence ratio of unburned gas. Metha and Das add to general operating parameters, as fuelling rate, compression ratio, engine speed and temperature, a dependence of soot emission also on spray mixing rate and air motion.

Semi-empirical models are, for instance, the two-step kinetic scheme for the formation of soot nuclei by Tesner et al. [7] and the more complex multi-step schemes by Surovikin [8] and by Fusco et al. [9]. The last two models account also for growth of nuclei to a critical diameter, where they become particles, and successive growth of these particles as being proportional to the surface area. Of wider diffusion is the model by Hiroyasu et al. [10], as it is, or with the successive modification of the oxidation rate made according to the Nagle and Strickland-Constable (NSC) model [11]: Arrhenius like expressions are adopted for both soot formation and oxidation rate and the net soot amount results as the difference between the two. Interest of these models is for the most related to the possibility of including them within multidimensional code simulating the whole working cycle of the engine, with a complete account of air motion, spray mixing rate, and local value of temperature, pressure and species concentration.

Soot models based on detailed chemistry [12, 13], are in course of assessment and only marginally applied to prediction of soot amount in diesel engines, due to the excessive computational effort required for their implementation.

The present work summarises some of the results obtained by coupling the use of optical measurements to the multidimensional engine modelling performed by means of a customised version of the KIVA-3 code [14], where the Hiroyasu et al. model is employed for soot formation and both the Hiroyasu et al. and the NSC models are supplied for oxidation. The latter model results to be particularly attractive if the consideration is made that it includes information regarding the particle size. This quantity is indeed recovered, within the present work, by simultaneous extinction and scattering measurements performed on an optically accessible diesel engine. This is characterised by low particulate emission because a strong air motion is forced in an external combustion chamber, which allows a strong prevalence of the premixed stage of combustion with respect to the non-premixed one.
The engine used in this study was, indeed, realized by modifying a single cylinder, air-cooled, 4-stroke diesel engine, having a displacement of 750 cm$^3$, a bore of 100 mm and a stroke of 95 mm. An external combustion chamber was realised and connected to the main chamber by a tangential duct. The standard piston having a toroidal bowl was replaced with a flat one and the chamber was set on the top side of the cylinder. The compression ratio was increased to 22.3:1 to compensate the increased heat losses consequent the realisation of the external chamber. This last, in its final configuration, has a volume equal to the real engine piston-bowl, namely 21.3 cm$^3$, and three optical windows, two in the longitudinal direction ($\Phi = 30$ mm) and another in the orthogonal direction ($w = 10$ mm and $h = 40$ mm). The chamber is equipped with a single hole (diameter of 0.34 mm) nozzle, centrally located on the top.

Measurements of diesel combustion are performed at an engine speed of 2000 rpm (at this speed, 1° crank angle corresponds to 83.3 $\mu$s), using commercial diesel fuel and varying start of injection. A low load fuel supply is considered with an injected mass per stroke equal to 0.0096 g. A series of tests is performed at a higher load, with an injected mass per stroke equal to 0.0128 g. Although slightly lower than for real working conditions, the values chosen of the injected mass avoid the obscuring effect of soot on the optical windows.

Start of fuel injection (SOI), defined as the crank angle where the injector needle lift is the 5 % of its maximum value, is at 12.8° before the top dead centre (BTDC). Pressure start of combustion (PSOC), as measured by a minimum in the rate of change of the indicated pressure, occurs 7° BTDC. Further details and specifications of the engine testing conditions are reported in ref. [15].

Broadband extinction and scattering measurements, from the ultraviolet (UV) to visible region, are performed on the divided chamber of the engine, in order to evaluate the soot particles diameter and volume fraction. These two quantities are followed with respect to time over the whole chamber volume. Details of the procedure for data analysis are given in ref. [16].

NUMERICAL SIMULATION

The numerical simulation of the engine under study is performed using a customized version of the KIVA-3 code [14], working on a mesh of 44367 cells. At the beginning of the computation the air pressure, temperature and turbulent kinetic energy are assumed to be uniform through the chamber, the duct and the cylinder, and are chosen according to experimental data. The ratio between the equivalent solid-body angular velocity of the fluid around the cylinder axis and the crankshaft angular rotational speed is assumed to be equal to zero. The value of the ratio between the equivalent solid-body angular velocity of the fluid within the combustion chamber around its axis and the crankshaft angular rotational speed, results from computation in the absence of fuel spray and is equal to about 90. This was shown in a previous paper to be in agreement with experimental data [17].

In the phase of code assessment various spray break-up models were tested and results compared with images recorded by UV-visible light absorption of refs. [17-18]. Not only using tetradecane in the simulation, as in ref. [17], but also using diesel fuel (df2 of KIVA), it was found that the best performance, from the numerical point of view, is obtained by using the model by Reitz [19], with values of the involved constants chosen accounting for experimental findings.

As regards chemical aspects, the low temperature reactions are simulated by means of the Shell model [20]. After definition of a cut-off value for temperature, pre-ignition following a degenerate branching chain reaction is assumed to occur at grid points where the value of this variable is lower than threshold. By exploiting the similarity observed in the pre-flame reactions of different diesel fuels, the auto-ignition process is hypothesised as occurring in eight steps involving five chemical species, three of which, R, B and Q, are fictitious and not suitable of a specific identification: R is the radical formed from the fuel, B is the branching agent and $Q$ a labile intermediate species. Involved constants are tuned by exploiting the analogy between the concentration of the fictitious species entering the reduced kinetic scheme and the emission intensity of radicals of appreciable concentration revealed by chemiluminescence spectra [18].

Soot formation is modelled according to the semi-empirical correlations of Hiroyasu et al. [10]. Two models are instead considered for oxidation, namely the one found in the same ref. [10], and the one by Nagle and Strickland-Constable [11]. The Nagle and Strickland-Constable model has the peculiarity to explicitly include quantities characterising the size of particle formed within the combustion chamber, besides accounting for mixture thermodynamic variables.

NO formation is predicted according to the Zeldovich model, where a calibration factor is considered according to literature [22].

RESULTS AND DISCUSSION

Since soot particles form as a consequence of the high temperature pyrolysis of burning hydrocarbons, the soot nucleation or inception stage takes advantage of fuel rich conditions, which are locally realised in regions placed close to
the liquid jet. As combustion proceeds, soot particles experience collision and surface growth while spreading throughout the whole chamber.

Transmission electron microscopy identifies mature soot as aggregates composed of nearly spherical primary particles or spherules. The formation of spherules should precede that of aggregates, whereas the transition from spherical to more complex shapes may be due to the fact that the particles are composed of viscous matter completely coalescing at small sizes but not having sufficient time for fusion as particle size increases, or to the cessation of surface growth. A part of them is oxidised by the surrounding leaner atmosphere, and only a small amount is found in the exhaust gases.

Assuming spherical particles, the procedure of evaluation of the particle diameter leads to the results of figure 1. Elaboration refers to experimental data collected in the region of inception of the soot formation process, in two load conditions considered. Note that the predicted diameter stays lower that 10 nm in the leaner case and not exceeds 20 nm in the richer one.

**Figure 1 -** Particles diameter evaluated in low load (circle) and high load (square) condition [16].

**Figure 2 –** Experimental and numerical soot volume fraction.

**Figure 3 -** Numerical soot volume fraction for different values of the soot diameter.

In order to show the capability of the employed numerical code in simulating the soot formation process and to highlight how modelling is affected by experimental information, the total soot concentration within the combustion chamber is followed with respect to time and compared to the soot concentration derivable experimentally, by multiplying the soot volume fraction for the particle density. The case of low load conditions is discussed referring to figure 2. Numerically computed curves are reported as computed with the model of Hiroyasu et al. [10] and with the model of Nagle and Strickland-Constable [11]. Using same values of constants in the NSC model as for the model of Hiroyasu, a value of the soot particles diameter equal to 30 nm and a particles density equal to 2.0 g/cm$^3$, as in ref [22], led to too-high values of the soot concentrations. It is, indeed, well recognised that the NSC model gives higher values of the peak in-chamber soot concentration with respect to the model of Hiroyasu et al., mainly because the NSC model is designed for oxygen partial pressure lower that in engine like conditions [22]. Another reason for over-prediction of in-chamber soot amount, not
highlighted in previous literature, lies in a not correct choice of the particles density and diameter. The mean value of this last, indeed, is shown in figure 1 to stay around the value of 8 nm, whereas the more realistic value of density of 1.8 g/cm$^3$ has to be taken. Dashed curve of figure 2 is obtained by using these values and also by reducing activation energies of soot oxidation of the 5% to take into account the stronger oxidising action in the actual conditions with respect to the case of ref. [22]. The pre-exponential factor for soot formation is also changed and set equal to 100.

The effect of the choice of the value of particle diameter on the results of the numerical simulations is shown in figure 3, where the curve computed by means of the model of Nagle and Strickland-Constable for a diameter of 8 nm is compared to the one obtained by changing this quantity to 30 nm and an intermediate value of 20 nm. It is evident that the higher is the diameter, the higher is the peak of soot concentration within the combustion chamber.

Spatial distributions of the numerically computed soot amount within the combustion chamber and of the experimental measurements are shown in figure 4 and 5, respectively. Two crank angles are considered. Soot is first localised in the region of the chamber individuated as the richer one, whereas, successively, it spreads throughout the whole chamber filling the entire volume. In discussing these images one has to take into account that the numerical simulation is able to furnish data over any chosen plane, as the middle one, while the two-dimensional experimental reconstructed image is, in some sense, averaged over the optical path. Slight differences results due to the fact that peripheral zones give a not appreciable contribute to soot formation.

In order to highlight the successive phases of the soot formation process within the entire engine under exam, an iso-value surface of soot concentration ($5 \times 10^{-6}$ g/cm$^3$) is drawn over the computational grid at different instants of time in figure 6. As expected, soot particles formed within the chamber are drawn through the duct and enter the cylinder while oxidation proceeds.
Figure 6. Numerically computed iso-value ($5 \cdot 10^{-6}$ g/cm$^3$) surface of soot concentration at various crank angles.

Figure 7 – NO concentration in the three zones of the computational volume compared with value at exhaust.
NO concentration, as predicted by the Zeldovich model in the three volumes of the computational grid, namely the main cylinder, the tangential duct and the divided combustion chamber, is represented in figure 7. Also in this case, pollutant starts to form within the combustion chamber and, subsequently spreads in the tangential duct and the main cylinder. Value of NO concentration measured at the exhaust is also reported as a cross in figure 7 and compared to the final value of the total amount of NO as evaluated by adding the three partial quantities. A correction factor was introduced to convert NO value in NO\textsubscript{x} according to ref. [22].

REFERENCES