National University of Science and Technology POLITEHNICA Bucharest

Doctoral School of the Faculty of Mechanical Engineering and Mechatronics

DOCTORAL THESIS – ABSTRACT

Research on the possibilities of improving performance, economy, and pollutant emissions of compression ignition engines by using nanoparticle-doped fuels

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Doctoral field: Mechanical Engineering

Bucharest

2026

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1. Use of nanoparticles as fuel additives

Chapter 1 began with the presentation of the general aspects regarding nanoparticles and with the description of the mechanisms through which they produce effects when used as additives for fuels intended for compression ignition engines.

Ultrafine particles with diameters between 1 and 100 nm are considered nanoparticles [1]. They exhibit a high ratio between the number of atoms concentrated at the surface of the material and the number of atoms in the interior, this value increasing as the size of the nanoparticles decreases. A high value of this ratio causes the properties of the nanoparticles to be similar to those of surface atoms. Thus, their reactivity and catalytic activity are intensified [2].

Nanoparticles can be classified into two categories: energetic or non-energetic [3]. Energetic nanoparticles participate directly in the exothermic reactions in the combustion chamber, contributing to an increase in the total amount of energy released. This category includes carbon-based nanoparticles, as well as certain core@shell structures, in which the metallic core is coated with an organic layer that enables participation in exothermic reactions. Non-energetic nanoparticles, mainly represented by metal oxides, do not burn together with the fuel, but they significantly influence the combustion process by releasing oxygen from their structure, thereby promoting oxidation reactions, with a positive effect on pollutant emission levels [4].

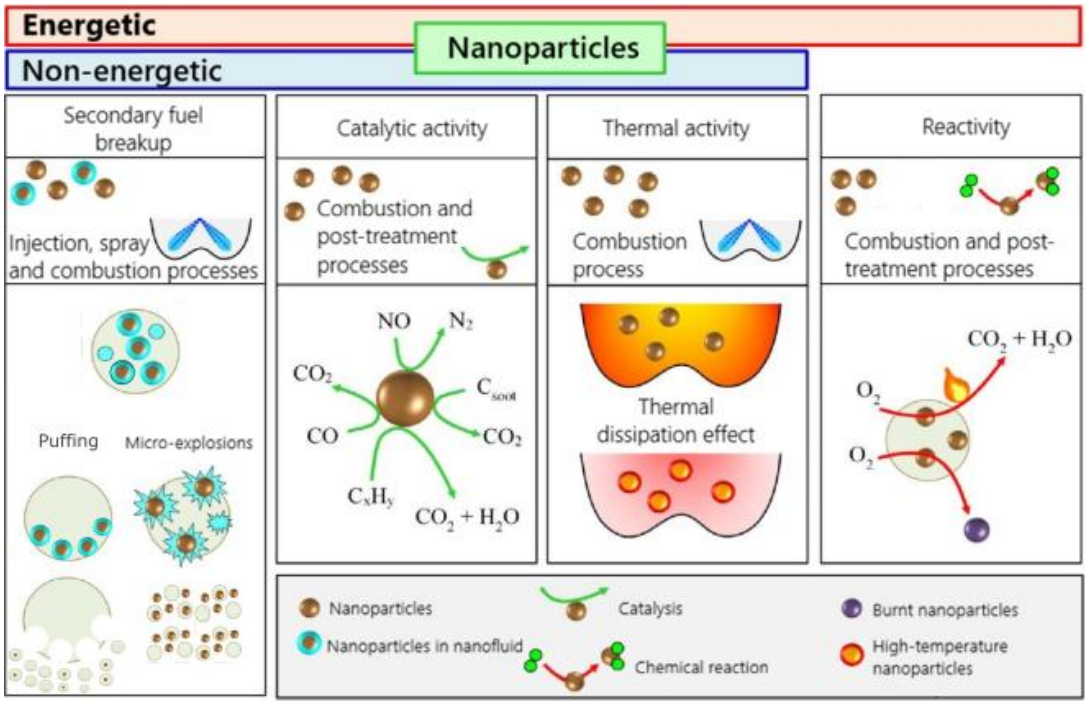


Figure 1. Influences generated by the use of nanoparticles in the Diesel engine [3]

In Figure 1, the influences generated by the use of nanoparticles in the Diesel engine are presented. Both energetic and non-energetic nanoparticles can influence the secondary breakup process of the fuel (through puffing and micro-explosions), exhibit catalytic activity, and lead to the occurrence of a thermal dissipation effect. In contrast, only energetic nanoparticles actively participate in the combustion process (in the exothermic reactions). All these mechanisms were described in the first part of Chapter 1.

Subsequently, based on the information available in the specialised literature, several summary tables were developed for metal oxide, non-metallic, core@shell, hybrid and multiple nanoparticles regarding:

- **The preparation of fuels with nanoparticle additives** (types of nanoparticles used, their size and dosage; base fuels; synthesis methods or suppliers from which they were procured; mixture preparation methods; characterisation procedures; solvents and surfactants used; and aspects related to stability) – four summary tables based on references [4–31];
- **The variations of certain physico-chemical properties of fuels with nanoparticle additives** (density, dynamic or kinematic viscosity, lower heating value, cetane number or cetane index, flash point and pour point) – nine summary tables based on references [4,6–12,14–16,19,21,23,24,29,31];
- **The effects on pollutant emission levels, performance and fuel economy of Diesel engines** – six summary tables based on references [4–7,9–11,13–17,19–26,28–31].

Based on the data extracted from the specialised literature regarding **the preparation of fuels with nanoparticle additives**, several general observations were formulated. The nanoparticles used may either be purchased from specialised suppliers or synthesised in the laboratory, being characterised by a variety of methods that allow the determination of the crystalline phase, chemical composition, morphology, optical behaviour and particle size distribution. They may be used in powder form or as nanofluids, by dispersion in a solvent. In the studies considered, various base fuels were blended with nanoparticle additives, however, biodiesel was the most frequently used, either in pure form or blended with diesel fuel. The adopted dosages were, in most studies, between 10 ppm and 150 ppm, higher concentrations being able to cause nanoparticle agglomeration, with negative effects on pollutant emissions, performance and fuel economy of Diesel engines. The preparation of nano-fuels generally involved mechanical, magnetic or ultrasonic homogenisation procedures with different

durations, their stability being variable and dependent on the type of nanoparticles, dosage, preparation method, and the use of solvents or surfactants.

The analysis of **the variations of certain physico-chemical properties of fuels with nanoparticle additives** generally revealed slight density variations, on the order of 0.1–0.4%. Kinematic or dynamic viscosity showed more pronounced variations, with both significant and moderate increases, as well as decreases, mainly influenced by the type and concentration of nanoparticles. The lower heating value recorded, in most cases, slight to significant increases, possibly associated with an influence of the nanoparticles on the amount of condensed water during the experimental determinations. Furthermore, the addition of nanoparticles generally led to an improvement in auto-ignition quality, reflected by increases in the cetane number and cetane index. Flash point and pour point values may experience both increases and decreases, these variations being strongly dependent on the type of nanoparticles and on the presence of solvents or surfactants.

Regarding **the effects on pollutant emissions, performance and fuel economy of Diesel engines**, most studies indicated simultaneous reductions in nitrogen oxides (NO_x), particulate matter and carbon monoxide (CO) emissions. At the same time, increases in thermal efficiency, brake power or torque (in studies where thermal efficiency values were not reported), as well as reductions in specific fuel or energy consumption, were reported. The observed trends confirmed that the use of nanoparticles as fuel additives for Diesel engines has the potential to reduce pollutant emission levels and to improve engine performance and fuel economy.

In Chapter 2, those types of nanoparticles reported in studies [7], [14] and [30] (MgO – magnesium oxide, MWCNT – multi-walled carbon nanotubes, CeO_2 – cerium dioxide) that led to the greatest reductions in pollutant emissions (NO_x, particulates and CO), together with improvements in performance and fuel economy of compression ignition engines, were considered. Although the hybrid nanoparticles used in [28] (CeO_2 + MWCNT) resulted in significant reductions in pollutant emissions, they were not considered further due to the difficulty related to their synthesis or procurement. Instead, Al_2O_3 (alumina) nanoparticles were also taken into consideration, as they are the most widely used metal oxide nanoparticles.

2. Study of the effects of adding nanoparticles to fuels on their physico-chemical properties and the influences induced on spray development

In the first part of Chapter 1, the effects of nanoparticle addition to fuels were presented. Among these, particular attention is given to the influence that they exert on fuel spray development. Thus, Chapter 2 addressed this research topic.

The development of the fuel spray in the combustion chamber of a Diesel engine can be evaluated by determining the characteristics of the fuel spray. Therefore, the main characteristics of the fuel spray were defined and the phenomena occurring during its development were described. According to study [32] these characteristics may be macroscopic, microscopic and atomisation-related. The macroscopic spray characteristics refer to global parameters, such as the spray cone angle and penetration. The microscopic characteristics refer to the properties of the fuel droplets, such as mean diameter, velocity and their size distribution. Atomisation characteristics include the break-up length and the break-up time of the liquid fuel jet into droplets.

Furthermore, those physico-chemical properties relevant to fuel spray development were defined, and their relationship with essential parameters such as jet break-up time, penetration, spray cone angle, Sauter Mean Diameter and the start of injection timing was highlighted. The observations showed that variations in the considered physico-chemical properties exert a similar influence on fuel spray development. An increase in density, viscosity, surface tension and bulk modulus leads to an increase in jet break-up time, penetration and Sauter Mean Diameter, respectively to a decrease in the spray cone angle and an advance shift of the start of injection timing in the case of mechanical injection systems.

Subsequently, the impact of Sauter Mean Diameter, penetration and spray cone angle on the performance, fuel economy and pollutant emissions of compression ignition engines was investigated. The observations made suggested that an ideal fuel spray is characterised by droplets with the smallest possible Sauter Mean Diameter, as well as by penetration and spray cone angle values appropriate to the dimensions of the combustion chamber. These characteristics favour more efficient combustion, which leads to improved engine performance and fuel economy, as well as reduced emissions associated with air–fuel mixture inhomogeneity and incomplete combustion (unburned hydrocarbons – HC, CO, soot and particulates). However, NO_x emissions will increase.

Finally, a literature review was carried out regarding the influence of MgO, CeO_2, MWCNT and Al_2O_3 nanoparticles, as well as of the surfactants used, on the physico-chemical properties of base fuels relevant to spray development (**density, viscosity, surface tension**). In addition, the bulk modulus was identified as another relevant physico-chemical property; however, no studies were found that provided values for this parameter in the case of fuels with nanoparticle additives. Thus, based on references [8,33–68], five summary tables were prepared in which the physico-chemical property values before and after the addition of the considered nanoparticles were centralised, together with the resulting percentage differences. Based on the calculated percentage differences, nine figures were subsequently produced, and the observed trends were discussed.

The analysis of the data from the specialised literature indicated that the impact of MgO, Al_2O_3, MWCNT and CeO_2 nanoparticles on fuel **density** is generally low due to the dosages in the ppm range. In most cases, the density variations were insignificant. However, there were cases in which larger variations were reported, these being attributed to the possible use of surfactants or solvents in high concentrations.

Regarding **kinematic viscosity**, the addition of MgO, Al_2O_3, MWCNT and CeO_2 nanoparticles to fuels produced notable effects; however, a single and predictable trend could not be established for all situations. In most cases, the addition of nanoparticles led to an increase in viscosity, suggesting that nanoparticles, through dispersion, create interactions that strengthen the fluid structure. Nevertheless, cases of significant decreases were also reported. The variability of the effects was strongly influenced by the composition of the fuel used, the nanoparticle dosage, their type and the presence of surfactants, which may amplify or attenuate the impact on viscosity. Correlations between decreases in viscosity and density were also observed in the context of the addition of metal oxide nanoparticles.

The addition of Al_2O_3, MWCNT, and CeO_2 nanoparticles to fuels influenced the **surface tension**, suggesting a general tendency toward modification of the fuels' surface properties. In most cases, the addition of nanoparticles led to an increase in surface tension. However, there was also a study [50] in which the surface tension decreased significantly when B20 contained MWCNT at dosages of 25, 50 and 100 ppm. Nanoparticle size proved to be an important factor, larger nanoparticles having a more pronounced impact on surface tension. Moreover, surfactants such as CTAB and oleic acid had a variable effect on surface tension, influencing the interaction between nanoparticles and fuel, but without producing significant changes.

3. Preparation methods, determination of certain physico-chemical properties and evaluation of the stability of fuels with carbon nanotube nanoparticle additives

The variations observed in the density and viscosity of the fuels following the addition of MgO, CeO_2, MWCNT and Al_2O_3 nanoparticles in Chapter 2 did not show a clear and uniform trend; therefore, it was considered necessary to continue the research by carrying out experimental determinations. Thus, within Chapter 3, the values associated with these physico-chemical properties were determined and compared for the fuels B7 (commercial diesel fuel), B7S5 (95% B7 and 5% n-butanol), respectively B7S5C25, B7S5C50 and B7S5C100 (B7S5 + 25, 50 and 100 ppm non-functionalised MWCNT, respectively), as well as B7S5C100-S (B7S5C100 + 1% by mass Span 60, relative to n-butanol).

The use of MWCNT-type nanoparticles was chosen because they are carbon-based structures. MgO, CeO_2 and Al_2O_3 are metal oxide nanoparticles, and these will be found in the engine exhaust gases and present significant risks when released into the environment. The non-functionalised MWCNT nanoparticles were purchased from SkySpring Nanomaterials, Inc., United States of America. They were produced by catalytic chemical vapour deposition and have a purity greater than 95%, an outer diameter of less than 8 nm, an inner diameter between 2 and 5 nm, and a length of 5–20 μm.

n-Butanol ($C_4H_{10}O$) was used as a solvent to facilitate the dispersion of the nanoparticles and to ensure optimal homogenisation of the mixture. It presents significant advantages compared with alcohols with shorter hydrocarbon chains, such as methanol (CH_3OH) and ethanol (C_2H_5OH), when blended with diesel fuel. These advantages include superior miscibility, a reduced tendency to absorb water (low hydrophilicity), and physico-chemical properties closer to those of diesel fuel [69].

For the preparation of the B7S5C100-S fuel, the use of the Span 60 surfactant was selected. In choosing this surfactant, the hydrophilic–lipophilic balance (HLB) was considered. HLB is a parameter used to describe the balance between the hydrophilic components (water-soluble) and the lipophilic components (oil-soluble) of a surfactant. HLB values range on a scale from 0 to 20. Surfactants with HLB values below 10 are predominantly lipophilic, having an affinity for oily substances, and this effect becomes more pronounced as the value decreases. On the other hand, surfactants with HLB values above 10 are predominantly hydrophilic, having a

greater affinity for water. In the case of Span 60, the HLB value is equal to 4.3, which makes it suitable for use in diesel fuel [70].

The addition of nanoparticles to a diesel–biodiesel blend, using n-butanol as a solvent, represents an element of novelty, since among the cited bibliographic studies only study [21] reported the BB40 fuel (60% biodiesel + 40% n-butanol) containing graphene oxide (GO), graphene nanoplatelets (GN) and MWCNT nanoparticles, using n-butanol as a solvent.

Furthermore, the refractive index was determined for all the fuels considered, and the stability of the fuels B7S5C25, B7S5C50 and B7S5C100 was evaluated by DLS-type tests (Dynamic Light Scattering).

The preparation procedure of the fuel blends B7S5, B7S5C25, B7S5C50, B7S5C100 and B7S5C100-S was described in detail in the doctoral thesis. In the case of fuels containing nanoparticles, this included the use of a Sonics Vibra-Cell ultrasonic homogeniser and an Ultra Turrax mechanical stirrer.

For determining the density of the fuels, a pycnometer was used. Determination with the pycnometer is a method frequently used for establishing the density of petroleum products. Viscosity determination was carried out with an Ostwald viscometer. This is also known as a capillary viscometer and is used to determine the viscosity of a liquid with known density [71]. The refractive index of the fuels was determined with an Abbe Krüss AR-2 refractometer. The DLS analyses were performed using the Beckman Coulter N4 Plus equipment, capable of determining particle sizes suspended in liquid between 3 nm and 3 μm. It is equipped with an optical system that includes six optical fibres arranged at fixed angles for light scattering detection (14.9°; 20.6°; 30.4°; 40.2°; 50.4° and 90°). These allow a multi-angle analysis of the particles, improving measurement accuracy [72].

Figure 2. A illustrates the fuel density values at temperatures of 15 °C and 40 °C, together with the relative differences calculated for the fuels containing nanoparticles, taking the base fuel (B7S5) as reference. The experimental results show that all prepared fuels present densities at 15 °C within the range imposed by the SR EN 590:2022 standard for diesel fuel marketed during the transition period (815–845 kg/m³). The calculated relative differences confirm the previously reported observations, indicating a reduced impact of nanoparticles on density, explained by the very low dosages used.

Figure 2. B presents the kinematic viscosity values of the fuels at 40 °C, the calculated mean values and the relative differences for the fuels containing nanoparticles, taking the base fuel (B7S5) as reference. The presence of n-butanol in the composition of the B7S5 blend leads to

a 9.24% reduction in viscosity compared with B7. The addition of 25 ppm MWCNT results in a further 2.21% reduction in viscosity, while at higher concentrations a slight increase is observed, namely 2.77% for 50 ppm and 2.56% for 100 ppm. In the case of the B7S5C100-S fuel, the use of the Span 60 surfactant leads to a 1.99% reduction in viscosity. All analysed fuels fall within the viscosity limits specified by the SR EN 590:2022 standard (2–4.5 mm²/s). The improved stability of the samples is essential to ensure uniform fuel flow through the capillary tube during the determinations, and the addition of Span 60 led to a lower dispersion of the kinematic viscosity values, indicating improved stability of the B7S5C100-S fuel compared with B7S5C100.

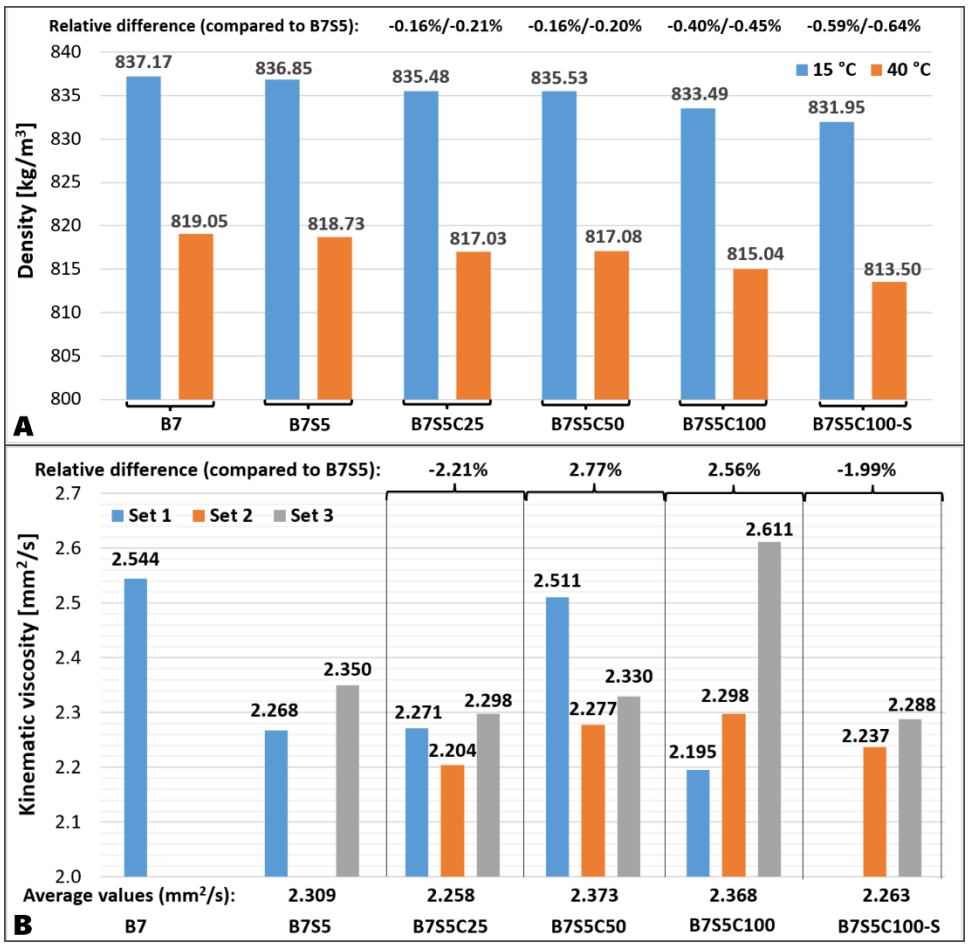


Figure 2. A. Density of the fuels at temperatures of 15 and 40 °C. B. Kinematic viscosity of the fuels at a temperature of 40 °C

Regarding the refractive index, the determined values were very similar for all the fuels investigated, suggesting that both the addition of n-butanol, as well as the presence of nanoparticles at low concentrations and the use of the Span 60 surfactant, do not significantly influence this optical property.

DLS measurements indicated good stability of the nanoparticle-containing fuels at concentrations of 25 and 50 ppm. At a dosage of 100 ppm, stability can be improved either using functionalised nanoparticles or through the addition of the Span 60 surfactant.

4. Experimental study in a closed experimental chamber regarding the determination of the macroscopic characteristics of the fuel spray

Chapter 4 continued the research through an experimental study carried out in a closed experimental chamber, aimed at determining certain macroscopic characteristics, such as penetration and spray cone angle, in the case of B7 fuel injection, at a pressure of 260 bar, in nitrogen (40 bar, 293 K), using a five-hole Delphi injector, which equips the UTB 2404055 Diesel engine.

In the initial part, the chapter included a bibliographic study carried out based on references [73–81], in which an experimental test rig for injection analysis was presented, as well as the theoretical considerations regarding the Schlieren technique, the essential stages of raw image processing and subsequent processing, and several results obtained by researchers on this topic.

Subsequently, the developed experimental rig (Figure 3) was presented, the angular distribution of the five fuel sprays was described, and the spray that developed in a plane parallel to the observation plane (the spray of interest) was identified. The operating parameters were described and several raw frames obtained during the experiments were presented. The procedure for frame pre-processing and processing in order to determine the variation of penetration and spray cone angle during injection was described. Finally, the obtained variations were discussed.

For the analysis of the distribution of the fuel sprays, a frame was captured through the discharge orifice of the experimental chamber, which was subsequently processed using a script developed in MATLAB. Since, in the frames obtained from the experimental determinations, two other sprays were present in the vicinity of the spray of interest, it was necessary to define a region within which the analysis was to be performed using another MATLAB script. Subsequently, a third MATLAB script was developed for the processing and analysis of these frames, with the objective of determining the axis of the spray of interest, the penetration, as well as the total area, respectively the area up to half of the penetration. For the conversion of the obtained results, another MATLAB script was developed through which the diameter of the experimental chamber window was determined in pixels, and subsequently conversion factors from pixels to mm for penetration and from pixels to mm^2 for area were calculated.



Figure 3. Experimental test rig for the study of fuel jet development

The analysis of the experimental results highlighted an asymmetric distribution of the fuel sprays. The temporal evolution of penetration (Figure 4. A) indicated a progressive increase up to the vicinity of the wall of the experimental chamber. The spray cone angle (Figure 4. B) exhibited high values at the beginning of injection, followed by a rapid decrease and subsequent stabilisation. The variations determined for penetration and spray cone angle in the case of the B7 fuel are similar to those determined in other experimental studies.

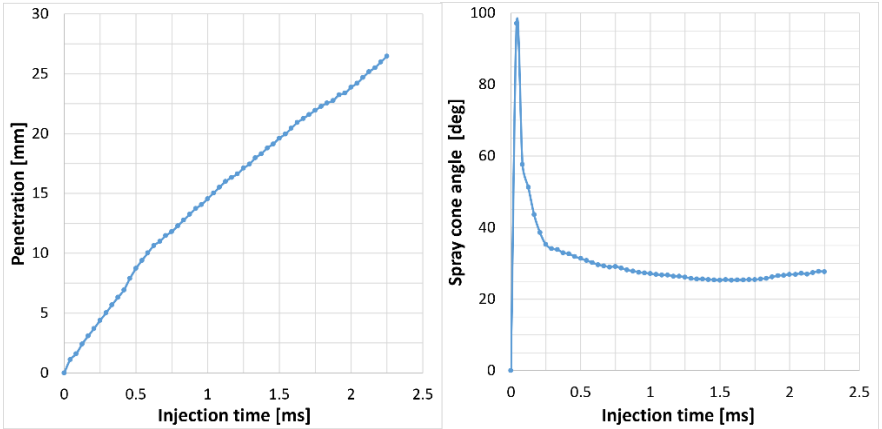


Figure 4. Variation of penetration (A) and spray cone angle (B) with injection time

The results obtained were used in Chapter 5 for the calibration of a CFD simulation model, which allowed the determination of the Sauter Mean Diameter for the fuels B7, B7S5, B7S5C25, B7S5C50 and B7S5C100, whose physico-chemical properties were determined in Chapter 3.

5. Determination by simulation of spray characteristics and mixture formation for fuels with nanoparticle additives

Chapter 5 includes two investigations carried out through numerical simulations aimed at determining the spray characteristics in the case of fuels with nanoparticle additives.

The first investigation consisted of a one-dimensional simulation performed in AVL BOOST Hydsim, used to analyse the spray development in the UTB 2404055 tractor Diesel engine during the ignition delay period at the engine's maximum power operating regime. Thus, in the model, the DP200 rotary distributor pump with plunger pistons, as well as the Delphi injectors that equip this engine, were taken into consideration.

The variations of penetration, spray cone angle and Sauter Mean Diameter were determined for two fuel blends: E20SF2 (78% diesel fuel, 20% ethanol and 2% 1-decanol surfactant) and MF15 (85% diesel fuel and 15% 2-methylfuran), containing CeO_2- and MWCNT-type nanoparticles at concentrations of 25, 50 and 100 ppm. The values of the physico-chemical properties of these fuels were taken from studies [8,55]. The calibration of the simulation model was carried out for the E20SF2 fuel based on the injector needle lift law and the pressure in the injection rail.

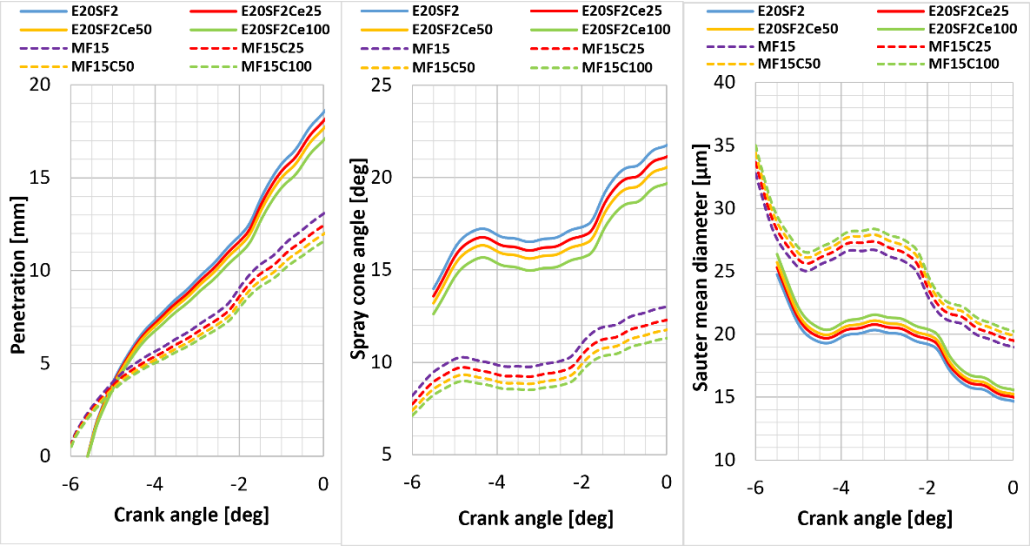


Figure 5. Variation of penetration, spray cone angle and Sauter Mean Diameter as a function of crankshaft position

The variations of penetration, spray cone angle and Sauter Mean Diameter as a function of crankshaft position (Figure 5) showed similar trends, regardless of the fuels used and the presence of nanoparticles. The addition of nanoparticles led to a reduction in penetration and spray cone angle, but also to an increase in the Sauter Mean Diameter for both fuels. The Sauter Mean Diameter, which is essential for the vaporisation process, exhibited decreasing values

with a quasi-linear trend, the highest values being recorded for the fuels with nanoparticle additives at the highest nanoparticle dosages.

Although several studies in the literature consider the addition of nanoparticles to be a method by which injection is improved, the obtained results showed that no improvement in atomisation is achieved in the case of fuels with nanoparticle additives. Furthermore, the higher values of surface tension and viscosity in the case of fuels with nanoparticle additives should have led to greater penetration compared with the base fuels. Thus, the need to use a multi-dimensional simulation model was considered essential, given the limitations of the one-dimensional model.

The second investigation involved the development of a multi-dimensional simulation model, within the ANSYS Fluent 2025 software (student version), for the closed experimental chamber, with the purpose of determining the Sauter Mean Diameter in the case of injections of B7, B7S5, B7S5C25, B7S5C50 and B7S5C100 over a period of 0.4 ms (approximately equal to the ignition delay duration of the UTB 2404055 Diesel engine at the maximum power operating regime). The configuration of the model was carried out based on the experimental data from Chapters 3 and 4, including fuel density and viscosity and the spray cone angle determined for B7. However, the surface tension values for the fuels without nanoparticle additives (B7 and B7S5) were taken from study [82], and subsequently the same percentage differences of surface tension variation for the addition of 25, 50 and 100 ppm MWCNT relative to the base fuel (B7S5) as those calculated in study [55] were applied. The model was calibrated according to the penetration variation determined experimentally for B7, and the validation of the results was carried out analytically by applying Elkotb's formula.

Initially, a brief bibliographic review was carried out regarding the working methodology, the considered parameters and the results reported. Subsequently, the geometry and discretisation of the developed model, the parameters used in the configuration, and the obtained results were presented.

The analysis of the obtained results indicated good model stability, all iterations reaching convergence at each time step. The penetration variation determined by simulation for the B7 fuel approached that obtained experimentally, which allowed the calibration of the numerical model based on the experimental data.

The evolution of the Sauter Mean Diameter during injection showed a rapid decrease in the initial phase, followed by a progressive reduction at a lower rate, this being in agreement with the results reported in the specialised literature.

Figure 6 presents the Sauter Mean Diameter values, determined both by simulation and analytically, at 0.4 ms from the start of injection for the fuels analysed in this study. In the upper part of the graph, the percentage differences between the values obtained by simulation and those calculated analytically are indicated. The analytical validation performed by applying Elkotb's formula confirmed the accuracy of the Sauter Mean Diameter estimation, the determined percentage differences being small for all the investigated fuels. Although the addition of nanoparticles increased surface tension at all dosages and viscosity at concentrations above 50 ppm, the advantage of using butanol as a solvent, which has lower viscosity and surface tension compared with those of the B7 fuel, was not eliminated. Thus, the Sauter Mean Diameter values for all the blends remained lower than those obtained for B7, indicating that fuel atomisation remained improved.

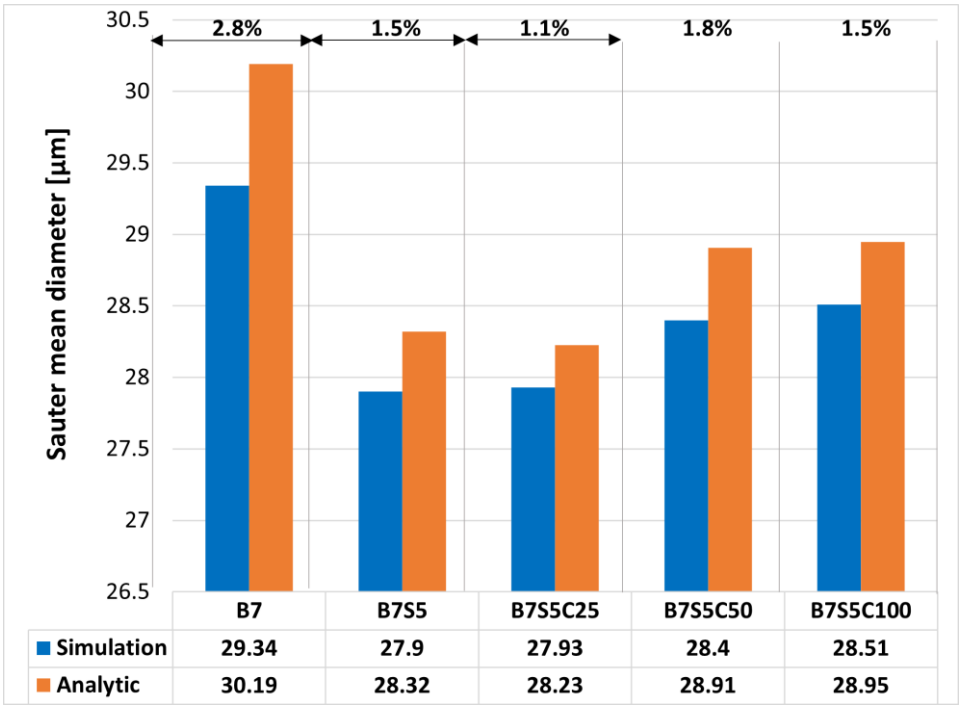


Figure 6. Sauter Mean Diameter at 0.4 ms from the start of injection (simulation vs analytical) for the fuels analysed

6. Experimental determination of the performance, fuel economy and pollutant emissions of a Diesel engine fuelled with alternative fuels with carbon nanotube nanoparticle additives

In this chapter, it was experimentally determined to what extent the fuels B7S5C25, B7S5C50 and B7S5C100 can lead to improvements in performance and fuel economy and to reductions in pollutant emissions of the UTB 2404055 tractor Diesel engine.

A description of the test rig, the operating procedure and the investigated operating regimes was carried out. The average variations of the ***rapidly varying parameters*** (pressure in the injection rail, injector needle lift law, heat release rate and in-cylinder pressure) were presented. In addition, the values of the ***slowly varying parameters*** recorded for each individual determination were presented, and the mean values of the performance, fuel economy and pollutant emission parameters obtained when fuelled with B7, B7S5C25, B7S5C50 and B7S5C100 were discussed.

The engine is installed in a test cell equipped with specialised equipment for carrying out the experimental investigations (Figure 7). The determinations were performed considering two engine operating regimes: the maximum torque regime (1400 rpm) and the maximum power regime (2400 rpm). At least five determinations were carried out for each fuel at both regimes.

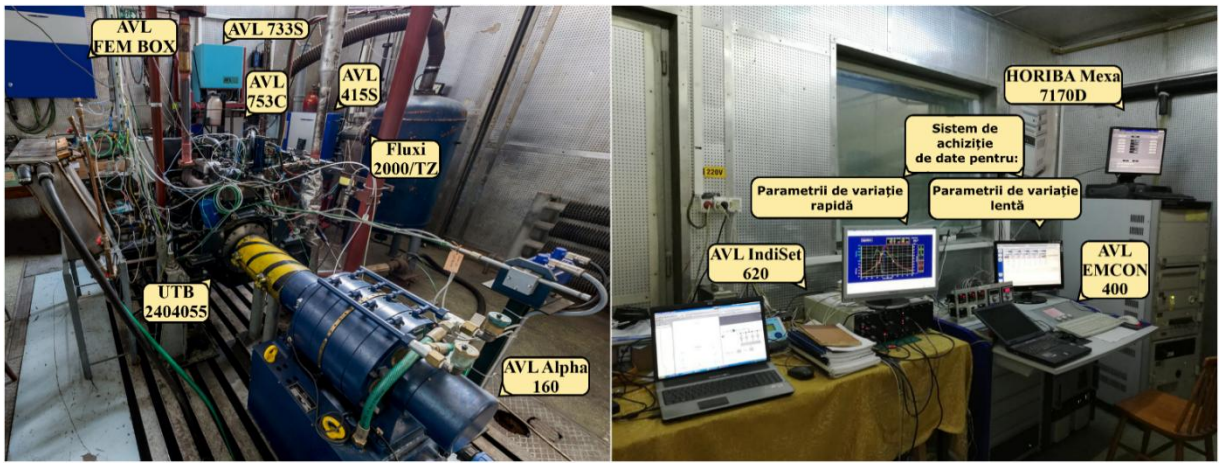


Figure 7. Engine test cell and control room

The addition of 5% n-butanol and non-functionalised MWCNT nanoparticles to commercial diesel fuel B7 did not produce significant changes in the evolution of the pressure in the injection rail at the maximum torque regime, while at the maximum power regime the observed influences were moderate. The minor differences identified in the injector needle lift laws were attributed to the modification of the physico-chemical properties of the fuels. For both operating regimes, increasing the nanoparticle dosage from 25 to 100 ppm led to an increase in the ignition delay and in the maximum value of the heat release rate, while the maximum in-cylinder pressure showed slight variations, without affecting the overall shape of the pressure diagram.

Figure 8 presents the values of brake thermal efficiency, HC and CO emissions, particulate concentration, NO_x emissions and smoke opacity recorded for the fuels B7, B7S5C25, B7S5C50 and B7S5C100, at the two operating regimes of the Diesel engine, at full load. The dosage of 50 ppm non-functionalised MWCNT nanoparticles proved to be optimal, ensuring

maximum engine operating efficiency. It resulted in notable increases in brake thermal efficiency at both considered operating regimes. At the maximum torque regime, it ensured minimum HC and CO emissions, a significant reduction in particulate concentration, and represented a compromise between the increasing trend of NO_x emissions and the decreasing trend of smoke opacity. At the maximum power regime, it ensured minimum values of CO emissions and smoke opacity, with reductions in HC emissions and particulate concentration, accompanied by a slight increase in NO_x emissions.

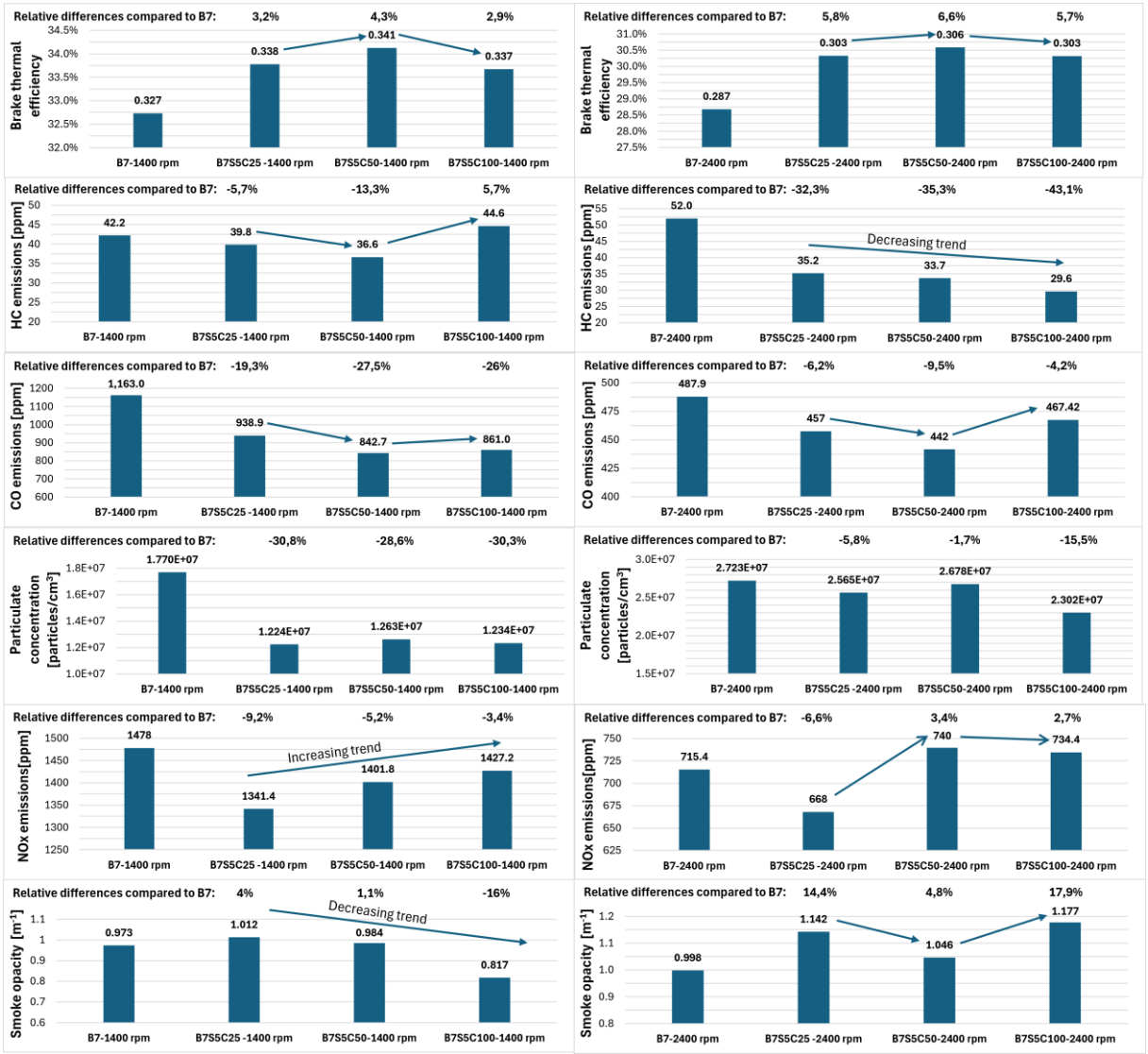


Figure 8. Values of brake thermal efficiency, HC and CO emissions, particulate concentration, NO_x and smoke opacity when fuelled with B7, B7S5C25, B7S5C50 and B7S5C100, for the two engine operating regimes: 1400 rpm – maximum torque; 2400 rpm – maximum power

7. Possible correlations between the operating regime characterised by performance, fuel economy and pollutant emission parameters and the dosages of carbon nanotube nanoparticles

Chapter 7 began with a literature review aimed at evaluating the effects of using fuels containing MWCNT nanoparticles on the fuel economy and pollutant emissions of Diesel engines. For this purpose, three summary tables were prepared. These were constructed based on bibliographic references [52,83–96] and include information regarding the base fuel, the values of brake thermal efficiency, brake specific fuel consumption, NO_x , smoke, HC and CO emissions, both before and after the addition of nanoparticles. In addition, the nanoparticle dosage, the stabilised operating regime at which the values were recorded, the commercial name of the engine used in each study, and the relative differences calculated considering the values reported for the base fuel as reference were mentioned. Based on the calculated percentage differences, six figures were subsequently prepared, and the observed trends were discussed.

The data indicated the existence of a tendency for an increase in brake thermal efficiency, a decrease in brake specific fuel consumption, and reductions in NO_x, smoke, CO and HC emissions after the addition of MWCNT nanoparticles.

Subsequently, correlations were established in order to highlight the influence of the dosage of non-functionalised MWCNT nanoparticles on performance (brake mean effective pressure), fuel economy (brake specific fuel consumption and brake thermal efficiency) and pollutant emissions (NO_x, smoke, HC and CO) of compression ignition engines, based on the data from studies [52,83–96] included in the conducted bibliographic research. Furthermore, it was investigated to what extent the experimental values from Chapter 6, determined at the two operating regimes of the UTB 2404055 Diesel engine, when fuelled with B7, B7S5C25, B7S5C50 and B7S5C100, approach the established correlations.

For each of the aforementioned parameters, four linear correlations were established as a function of dosage. The first correlation was determined by considering all the values corresponding to each individual dosage. The second correlation was obtained using the mean values corresponding to each dosage. The other two correlations addressed the effects of the addition of MWCNT nanoparticles: one was established based on all the percentage differences calculated for each dosage individually, and the other based on the mean percentage differences corresponding to each analysed dosage. Figure 9 presents, as an example, the correlations established for brake thermal efficiency.

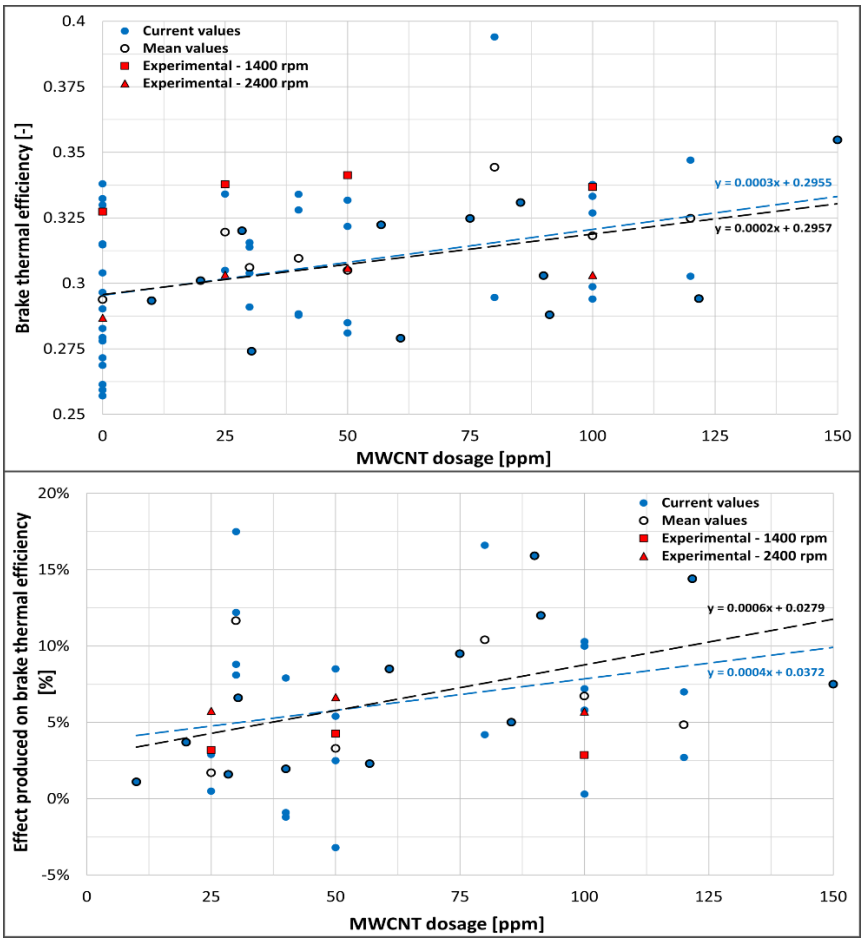


Figure 9. Correlations between the values of brake thermal efficiency, the effect produced on it and the dosage of MWCNT nanoparticles

Most of the experimental determinations in studies [52,83–96] were carried out at constant brake mean effective pressure. For this reason, the hourly fuel consumption values for the base fuels without nanoparticle additives were determined based on the known values of brake specific fuel consumption, and subsequently the hourly fuel consumption was considered constant, in order to allow the variation of brake mean effective pressure when using fuels with nanoparticle additives.

Since NO_x, HC and CO emissions were reported in the specialised literature [52,83–96] either in ppm or in g/kWh, only the studies that reported the values in ppm were considered for establishing the correlations, these being the majority. Furthermore, most studies reported smoke opacity values, but using different units of measurement (g/kWh, %, HSU or m^{-1}). Consequently, for the development of the correlations, all the reported values were converted into a common unit of measurement, namely m^{-1}.

The analysis of the established correlations highlighted, overall, a favourable influence of the MWCNT nanoparticle dosage on the performance, fuel economy and pollutant emissions

of compression ignition engines. Brake mean effective pressure showed a general increasing trend with MWCNT dosage; however, the experimental values obtained in this study did not reflect this increase, as the hourly fuel consumption was not maintained constant. In contrast, brake thermal efficiency increased with dosage, and the experimental results obtained at the maximum power regime were well aligned with the established correlations up to the 50 ppm dosage, identified as optimal. Brake specific fuel consumption showed a decreasing trend with MWCNT dosage, and the experimental results obtained confirmed this trend, with better agreement in the case of the maximum power regime and up to the 50 ppm dosage. Regarding pollutant emissions, the correlations for NO_x indicated different trends depending on the approach used, the differences being attributed to the high variability of the experimental data in the literature. However, the values obtained in this study approached the correlations based on mean values, especially at the maximum power regime. For smoke opacity, HC and CO, the correlations indicated a decreasing trend in emissions with increasing MWCNT dosage. In the case of smoke opacity, the experimental values obtained were lower than those estimated, and regarding the effects, a good correspondence with the correlation estimates was observed only at the 100 ppm dosage, for the maximum torque regime. For HC emissions, the values obtained approached the trend estimated by the correlation based on current values, and the percentage differences up to 50 ppm, at the maximum torque regime, were close to the linear regressions. In the case of CO emissions, the experimental values were aligned with the established correlations up to 50 ppm for both regimes, and at the maximum power regime the percentage differences for 25 and 50 ppm were the closest to the linear correlations.

8. Conclusions, contributions and recommendations for future research

Chapter 8 summarised the main results obtained within the doctoral thesis, highlighting the final conclusions, personal contributions and development directions for future research regarding the use of MWCNT nanoparticles as additives for Diesel fuels. The research integrated experimental and numerical studies, as well as bibliographic analyses, with the objective of evaluating the influence of the addition of nanoparticles on the physico-chemical properties of fuels, fuel spray characteristics, performance, fuel economy and pollutant emissions of compression ignition engines.

The experimental determinations regarding the physico-chemical properties of the fuels demonstrated that the investigated blends comply with the requirements of the standard for commercial diesel fuel, and the influence of nanoparticles on density is low, due to the dosages

used. The addition of n-butanol led to a decrease in kinematic viscosity, while the addition of MWCNT nanoparticles produced moderate variations, dependent on concentration. Stability evaluation by DLS tests confirmed adequate stability for concentrations of 25 and 50 ppm, and for higher concentrations the stability may be improved using the Span 60 surfactant or functionalised nanoparticles.

The analysis of the fuel spray, carried out in a closed experimental chamber, highlighted an asymmetric distribution of the sprays in the case of the utilised injector, as well as variations in penetration and spray cone angle comparable to those reported in the specialised literature. These results constituted the basis for the development and calibration of the multi-dimensional simulation model.

Within the thesis, two simulation models were developed for the analysis of fuel spray characteristics. The one-dimensional model highlighted the limitations of simplified approaches in evaluating the effects of the addition of nanoparticles on atomisation, while the multi-dimensional model, calibrated and validated based on the experimental data obtained in this study, allowed the estimation of the Sauter Mean Diameter, and the analytical validation confirmed the accuracy of the obtained results. The results showed that, although the addition of nanoparticles led to increases in viscosity and surface tension at certain dosages, the advantages of using n-butanol as a solvent were not eliminated, and the atomisation quality remained improved compared with the reference diesel fuel.

Following the experimental investigations carried out on the UTB 2404055 Diesel engine, fuelled with diesel fuel (B7) containing 5% n-butanol and non-functionalised MWCNT nanoparticles at various dosages, an optimal dosage of 50 ppm was identified, which ensured maximum brake thermal efficiency at both engine operating regimes and reductions in pollutant emissions in almost all cases.

The bibliographic research allowed the establishment of correlations between the MWCNT nanoparticle dosage and the performance, fuel economy and pollutant emission parameters of Diesel engines. These correlations indicated trends of increasing brake mean effective pressure and brake thermal efficiency, decreasing brake specific fuel consumption, as well as reductions in smoke, HC and CO emissions, while in the case of NO_x emissions a difference was observed between correlations based on values, which suggested a slight increase with dosage, and those based on effects, which indicated a decreasing trend. This discrepancy was attributed to the high variability of the experimental data caused by differences between engines, testing conditions and fuel types.

The personal contributions of the thesis consist of the preparation of fuels with nanoparticle additives, the determination of certain physico-chemical properties and the evaluation of their stability, as well as the development of an experimental rig that enabled the acquisition of images of the development of the B7 fuel spray injected into nitrogen, in a closed experimental chamber, using the Schlieren technique, followed by the application of specific image processing procedures. Two simulation models were developed for the analysis of the characteristics of fuel sprays with nanoparticle additives in the engine and in the closed experimental chamber, respectively. A Journal-type script was also developed for displaying the Sauter Mean Diameter values in the ANSYS Fluent console. Sets of experimental determinations were carried out on the UTB 2404055 Diesel engine, at two operating regimes, when fuelled with B7, B7S5C25, B7S5C50 and B7S5C100, each determination being repeated at least five times to ensure increased data reliability, in order to perform a comparative analysis of performance, fuel economy and pollutant emission parameters. Furthermore, correlations were established to highlight the influence of the dosage of non-functionalised MWCNT nanoparticles on the performance, fuel economy, and pollutant emissions of Diesel engines, based on data reported in the literature, and the extent to which the experimental values obtained in this study approached these correlations was subsequently analysed.

Finally, future research directions were proposed, aimed at improving the experimental rig for determining fuel spray characteristics by controlling the temperature of the nitrogen inside the experimental chamber and by implementing an electronic injection system. In addition, improvement of the one-dimensional simulation model is considered through the adoption of physico-chemical properties variable with pressure. Optimisation of the multi-dimensional simulation model may be achieved by increasing the nitrogen temperature in the experimental chamber to values as close as possible to those existing in the cylinders of a Diesel engine at the beginning of the injection process, as well as by defining the injected particles as "multicomponent", in order to allow a more realistic evaluation of the complex secondary breakup process, influenced by the occurrence of micro-explosions and the puffing phenomenon, both having a significant impact on fuel spray quality. In addition, the adoption of intermediate nanoparticle dosages between 50 and 100 ppm is envisaged, since the interval between these values may be too large and the optimal dosage could be located between them. At the same time, the use of MWCNT nanoparticles functionalised with OH groups is considered, as this could ensure improved stability in the mixture with n-butanol, with the potential to increase engine efficiency and reduce pollutant emissions.

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