Aerosol and Air Quality Research

ORIGINAL RESEARCH
https://doi.org/10.4209/aaqr.230281

Effect of Titania Nano-additives on Fine and Ultrafine Carbonaceous Emissions during Flame Combustion of Diesel

Special Issue:
Carbonaceous Aerosols in the Atmosphere (II)

Akshat Jain[1], Anirudha Ambekar[1,2], Thaseem Thajudeen[1,2,3*]

[1] School of Mechanical Sciences, Indian Institute of Technology Goa, Farmagudi, Ponda - 403401, Goa, India
[2] Center of Excellence in Combustion Sciences, Indian Institute of Technology Goa, Farmagudi, Ponda - 403401, Goa, India
[3] Center of Excellence in Particulates, Colloids and Interfaces, Indian Institute of Technology Goa, Farmagudi, Ponda - 403401, Goa, India

ABSTRACT

The severe impacts of emissions from combustion necessitate the need for advanced mitigation techniques. This study focuses on experimentally investigating the change in particulate matter (PM) emissions during the flame combustion of diesel blended with varying quantities of titania (TiO_2) nano-additives. The initial observations using a Scanning Mobility Particle Sizer showed a reduction in the total number concentration (TNC) of PM emissions for TiO_2-nanofuel samples compared to diesel. However, detailed investigations revealed the enhancement in the TNC of ultra-fine particles (UFPs) with mobility diameters less than 100 nm. This indicates the possibility of the emission of nano-additives during flame combustion, which enhances the number concentration of UFPs. The evolution of TiO_2 nanoparticles is validated by performing the elemental composition analysis using energy-dispersive X-ray spectroscopy after sampling the PM emissions. A detailed experimental study also revealed the significance of the size and stability of the dispersed nanoparticles in the overall emissions. Ball milling (BM) was used for the size reduction of dispersed nanoparticles to enhance the dispersibility of the nano-additives. BM, when combined with bath-sonication (BS), resulted in the highest reduction in the TNC (37.70% for Ti100 BM-BS, 48.46% for Ti150 BM-BS, and 53.27% for Ti200 BM-BS), highlighting the importance of size of the dispersed nanoparticles. The detailed analysis of UFPs showed an increase in the TNC of particulates in sub-23 nm (22.92% for Ti100 BS and 39.16% for Ti100 BM) and super ultra-fine (96.46% for Ti100 BS, 100.83% for Ti100 BM, and 16.73% for Ti100 BM-BS) regions for nanofuel samples in contrast to neat diesel.

Keywords: Ball milling, Combustion aerosols, Nano-additives, Particle size distribution, Ultra-fine particles

Received: November 17, 2023
Revised: January 28, 2024
Accepted: March 4, 2024

* **Corresponding Author:**
thaseem@iitgoa.ac.in

Publisher:
Taiwan Association for Aerosol Research
ISSN: 1680-8584 print
ISSN: 2071-1409 online

1 INTRODUCTION

Particulate and gaseous emissions from various combustion sources have far-reaching implications on indoor and outdoor air quality (Gaffney and Marley, 2009; Vardoulakis *et al.*, 2020). Pollutants generated during the combustion of diesel fuel typically comprise particulate matter (PM), carbon monoxide (CO), nitrogen oxides (NO_x), volatile organic compounds (VOCs), etc. Fine and ultra-fine particulates have an adverse effect on living beings and the environment (Maciejczyk *et al.*, 2021; Sher, 1998). Chronic exposure to PM emissions is associated with severe respiratory conditions like asthma, bronchitis (Walsh, 2014; WHO, 2018). Ultra-fine particles (UFPs) are even more severe in affecting human health as they can deeply infiltrate the respiratory system and penetrate the bloodstream, exacerbating other health issues such as cardiovascular diseases, gastrointestinal diseases, and neurological disorders (Cassee *et al.*, 2019; HEI, 2013; Sonwani *et al.*, 2021).

The transportation sector is a prominent source of particulate emissions due to its reliability on conventional fuels. Despite the prevailing options of alternative energy sources, diesel persists as the predominant fuel choice within the transportation sector. The compression ignition (CI) technology uses diffusive flame combustion where the imperfect mixing of fuel with air (oxidizer) leads to the formation of high concentrations of carbonaceous aerosols (Liu *et al.*, 2020). Over the last two decades, nanoparticles as additives in liquid fuels have been used, which improves the combustion characteristics of fuel and simultaneously reduces harmful emissions (Ben Said *et al.*, 2022; Tomar and Kumar, 2019). Nano-additives have a high specific surface area, leading to improvement in the heat transfer characteristics of the fuel. Additionally, nano-additives act as catalyst and enhance the combustion process, promoting better oxidation of fuel and resulting in the reduction of gaseous and PM emissions. The droplet combustion studies have also shown the phenomenon of more intense and frequent micro-explosions in the case of nanofuel compared to neat diesel (Mehrizi *et al.*, 2022). The micro-explosion of primary atomized droplets leads to secondary atomization that aids in the better mixing of fuel with air. This helps in better combustion of diesel fuel, leading to a reduction in unburnt hydrocarbon, carbon monoxide, soot, and other particulate emissions. Therefore, nano-additives, when blended with diesel, improve the thermo-physical properties and combustion characteristics of the fuel, also resulting in the reduction of PM and gaseous emissions (Dobrzyńska *et al.*, 2022; Sezer, 2019). The combustion process in the CI engine includes the spraying of fuel into the combustion chamber, mixing of atomized droplets with air, evaporation of liquid droplets into vapor, burning of air-fuel mixture, and the diffusive flame ignited around the sprayed droplets helps the chemical reaction to proceed further. Thus, the fundamental study of a diffusive flame consists of the spray injection characteristics, droplet evaporation characteristics, flame combustion characteristics, etc. Investigations have been done to study the benefits of adding nanoparticles to diesel and biodiesel blends on the CI engine characteristics (Basha *et al.*, 2022; Gad *et al.*, 2023). The experimental analysis of the droplet evaporation characteristics validates the phenomenon of micro-explosions during nanofuel combustion (Mehrizi *et al.*, 2022). Consequently, there is an improvement in the combustion phenomenon, leading to a reduction in PM and gaseous emissions. The diffusive flame characteristics during combustion are fundamentally studied through strand experiments. However, the elementary study of PM emissions for liquid fuel diffusion flame still needs detailed investigations. Additionally, the effect of blending nano-additives to diesel on PM emissions reduction and changing the number concentration of UFPs is quite essential.

Although various researchers have investigated the benefits of adding nanoparticles to diesel and diesel-biodiesel blends, very few studies have investigated the role of the primary particle size in the improvement of combustion and emission characteristics of the fuel (Ağbulut, 2022; Chinnasamy *et al.*, 2019; Dinesha *et al.*, 2021). However, none of the previous work has studied the actual size of particles/aggregates dispersed in diesel/biodiesel and its importance in the reduction of emissions. The aggregation of nanoparticles dispersed in diesel enhances the sedimentation process, and the benefits of adding nanoparticles get nullified over time. Therefore, the stability in terms of dispersibility of nanoparticles is an essential aspect that considers the shelf life of nanofuel. The particle size distribution (PSD) of the dispersed nano-additives aids in understanding the significance of the size of nanoparticles in the reduction of fine and ultra-fine particulate emissions. The reduction in the size of the dispersed nanoparticles using mechanical methods leads to improvement in the shelf life of nanofuel suspension.

The fundamental study of the flame combustion of fuel blended with nano-additives provides better insights for the reduction in particulate matter emissions. The experimental investigations showed the suppression of soot emissions from a propane diffusion flame with the addition of metal additives (Cotton *et al.*, 1971). There is the production of hydroxyl radicals, which rapidly remove soot or soot precursors. The results also showed that the soot reduction mechanism changes with the type of metal. Similarly, the sooting tendency increases for laminar pre-mixed ethylene-oxygen-argon flames with the addition of ferrocene particles (Hirasawa *et al.*, 2004). Both experimental and computational studies support the enhancement in soot formation as ferrocene particles provide a surface to initiate soot structure growth. Further, experiments were conducted to measure the soot emission from turbulent methane and propane diffusion flames using laser-induced incandescence (LII) (Canteenwalla *et al.*, 2007). The results show that the amount of soot formation depends upon fuel composition and the fuel flow rate through the burner. In addition, the research was carried out to analyze the effect of the addition of ethanol to gasoline on the soot formation in a co-flow diffusion flame (Matti Maricq, 2012). The study included the comparison of soot emissions with flame height, and the results showed the reduction in volatile organic compounds (VOCs) and soot primary particle size with the percentage increment of ethanol blended. The burning rate study of liquid monopropellants with and without additives was carried out using a quartz-lined cavity and steel tube (McCown *et al.*, 2014). The results for strand burner tube experiments showed an increase in burning rates by 60–70% with the addition of 1% silica and 5% aluminum to neat nitromethane. Furthermore, the experiments were performed to understand the growth of soot particles and polycyclic aromatic hydrocarbons (PAHs) at atmospheric pressure for fuel-rich propane/oxygen-diffusion flame with the addition of 0.1% and 0.2% ferrocene metal additives (Hu *et al.*, 2016). The results show that ferrocene reacts with O and OH radicals, aids in lowering the burner flame temperature, and restrains the growth of PAHs into larger aggregates. Additionally, there is better oxidation of soot particles at lower temperatures when fuel is blended with ferrocene additives. Similarly, soot particle size distribution for laminar pre-mixed burner-stabilized ethylene flames has been studied (Zhou *et al.*, 2023). The experimental and computational study shows enhanced particle coagulation and the growth in soot particle size with the addition of ferrocene additives.

The benefits of adding nanoparticles to reduce PM emissions are quite evident. However, the experimental studies for PM emissions, including UFPs, during diesel flame combustion need detailed investigations. The effect of the addition of nano-additives on the emissions of fine and ultra-fine particulate matter is still not well understood. The measurement of the number concentration of particulate emissions helps us to understand the physical mechanism behind the corresponding increase or decrease in PM emissions for the distinct size range. Although several studies across the world have looked into the overall effect of nano-additives in terms of PM concentration, combustion characteristics, etc., very few studies have attempted to understand the evolution of the nano-additives post-combustion and their impact on UFP emissions (Kegl *et al.*, 2021). Thus, the present study includes the qualitative and quantitative analysis of the PM emitted during the flame combustion of diesel with and without the addition of TiO_2 nano-additives, with a special focus on submicron-sized carbonaceous particles.

The strand experiments are significant in carrying out the fundamental studies for a better understanding of the combustion process. The experiments of PM emissions measurement were conducted in a controlled environment that allows the easy reproducibility of the data. The stability of nanofuel is also an essential aspect that needs a detailed study to effectively utilize the benefits of nano-additives for a long time. Consequently, this study focuses on the use of ball milling in altering the particle size distribution (PSD) of the TiO_2 nanoparticles dispersed in diesel. The dispersibility of nanoparticles helps to understand the shelf life of nanofuel. In this study, the experimental measurements of the PM emissions during the flame combustion of diesel were carried out using a Scanning Mobility Particle Sizer (SMPS) to understand the effect of nano-additives. The significance of the size and morphology of TiO_2 nanoparticles in the reduction of total PM emissions is investigated. Presently, the focus is on the impact of nanoparticles on the ultra-fine particulate emissions and the change in the number concentration of PM emissions in sub-23 nm (< 23 nm), super-ultra-fine (23–50 nm), and ultra-fine (50–100 nm) regions. The characterization of the PM emissions using field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDS) to investigate the evolution of nano-additives during flame combustion is also reported.

2 MATERIALS AND EXPERIMENTAL METHODS

The strand experiments were performed with diesel fuel (purchased from a local BPCL petroleum station). Titania (TiO_2) nanoparticles (average particle size, APS $\leq$ 25 nm) were purchased from Sigma-Aldrich Chemicals Pvt. Ltd., and their specifications are summarized in Table S1. The field emission scanning electron microscopy (FESEM) images and energy-dispersive X-ray spectroscopy

(EDS) analysis of titania nano-additives are presented in Fig. S1 and Table S2, respectively. TiO_2 nano-additives were blended into neat diesel in the quantity of 100 ppm, 150 ppm, and 200 ppm to prepare the nanofuel suspensions. TiO_2, being a metal oxide, acts as a catalyst and promotes better oxidation of fuel, leading to improvement in the combustion process. Therefore, TiO_2 nano-additives aid in the reduction of soot and other PM emissions. Since TiO_2 is known to be biocompatible and is safe for human health when exposed under standard conditions, its existence in PM emissions post-combustion might not present a health risk (Rashid *et al.*, 2021).

2.1 Nanofuel Sample Preparation

The nanofuel samples for experimental investigations are prepared by adding TiO_2 nanoparticles to diesel. The nanofuel suspension was hand-stirred to prepare a homogeneous mixture. When TiO_2 nanoparticles were blended with diesel, the particles tend to form aggregated structures, and the average size of the dispersed TiO_2 nanoparticles can be much larger than the APS mentioned in Table S1. Thus, Span80 (sorbitan monooleate) surfactant was added to diesel to hinder the aggregation of the dispersed nanoparticles. The addition of surfactant to diesel should not alter the properties of diesel significantly; therefore, the amount of surfactant added was twice that of the nano-additives. TiO_2 nano-additives were dispersed in diesel fuel and Span80 mixture in ppm (or mass percentage ratio). After hand stirring for 15 minutes, the nanofuel sample was ultra-sonicated for 60 minutes with the help of the Branson CPX3800H bath sonicator (BS), purchased from Emerson Electric.

The blending of nano-additives to diesel is beneficial due to the high specific surface area of the nanoparticles added. Consequently, the morphology of TiO_2 nanoparticles plays a vital role during the combustion of TiO_2-laden diesel nanofuel (Jeon *et al.*, 2015). Considering this, the size modification of the dispersed nano-additives was done using a mini-planetary twin-bowl holder ball mill MBM-07, purchased from InSmart Systems. The ball milling (BM) was done for 32 minutes, and the other input parameters used for BM the wet mixture of TiO_2 nano-additives, Span80, and diesel are given in Table S3. Once the BM operation was completed, the wet mixture was poured back into the bottle, hand-stirred for 15 minutes, and ultra-soniacted for 60 minutes.

For the stability analysis, particle size distribution (PSD) of the dispersed TiO_2 nano-additives was measured by the Dynamic Light Scattering (DLS) technique using a Zetasizer ZS90, purchased from Malvern Panalyticals. DLS measures the concentration of dispersed particles as a function of their hydrodynamic diameter (D_h). Due to the effect of rotational diffusion, PSD analysis was in terms of apparent hydrodynamic diameters and not true hydrodynamic diameters. The following naming of the test fuel samples is used throughout the manuscript:

1) Diesel (neat diesel)
2) Ti100 no-Sp BS (100 ppm TiO_2 + diesel, bath-sonicated)
3) Ti100 BS (100 ppm TiO_2 + 0.02% wt. Span80 + diesel, bath-sonicated)
4) Ti100 BM (100 ppm TiO_2 + 0.02% wt. Span80 + diesel, ball-milled)
5) Ti100 BM-BS (100 ppm TiO_2 + 0.02% wt. Span80 + diesel, ball-milled, bath-sonicated)
6) Ti150 BS (150 ppm TiO_2 + 0.03% wt. Span80 + diesel, bath-sonicated)
7) Ti150 BM (150 ppm TiO_2 + 0.03% wt. Span80 + diesel, ball-milled)
8) Ti150 BM-BS (150 ppm TiO_2 + 0.03% wt. Span80 + diesel, ball-milled, bath-sonicated)
9) Ti200 BS (200 ppm TiO_2 + 0.04% wt. Span80 + diesel, bath-sonicated)
10) Ti200 BM (200 ppm TiO_2 + 0.04% wt. Span80 + diesel, ball-milled)
11) Ti200 BM-BS (200 ppm TiO_2 + 0.04% wt. Span80 + diesel, ball-milled, bath-sonicated)

The effect of the morphology of dispersed nano-additives on flame combustion is examined by comparing the fine and ultra-fine particulate matter emissions in the case of bath-sonicated and ball-milled nanofuel samples with diesel.

2.2 Properties of the Test Fuel Samples

The important thermo-physical properties of the test fuel samples are density (ρ) and calorific value (CV). The mass of TiO_2 nano-additives, surfactant, diesel fuel, etc., was measured using an electronic weighing balance (Radwag AS 220.R2, maximum load = 220 g). The density of diesel and nanofuel samples was calculated by measuring the mass of the known volume of fuel. The CV of test fuel samples was measured using a mLabs bomb calorimeter purchased from Labtronics. After the measurement of the properties of test fuel samples, the experiments were carried out for PM emissions measurement during flame combustion of TiO_2-laden diesel fuel.

2.3 Experimental Setup

The PM emissions study through strand experiments aids in understanding the effect of nano-additives on fine and ultra-fine particulates in a controlled way. The morphology of nanoparticles is an important factor that governs the improvement in thermo-physical properties and combustion characteristics of the fuel. Therefore, the size and structure of TiO_2 nanoparticles play a crucial role in the suppression of PM emissions during the flame combustion of diesel. To facilitate that, Span80 surfactant and mechanical methods (ball milling and bath sonication) were used for nanofuel preparation that helped to hinder the aggregation mechanism and size reduction of dispersed nano-additives, respectively.

The present study for strand experiments of flame combustion of diesel with the addition of TiO_2 nano-additives was carried out in a quiescent ambience at a standard temperature and atmospheric pressure (298.15 K, 1 atm.). The PM, including UFPs, emissions were measured with the help of a Scanning Mobility Particle Sizer (SMPS) purchased from TSI Incorporated. SMPS measures the PSD based on mobility diameter (D_m) and quantifies the variation in normalized number concentration with D_m of the particles present in the aerosol (PM emissions) inflow. Additionally, SMPS provides the total number concentration (TNC) of PM emissions for the measured size range. For the measurement of PM emissions, the hollow non-conducting tube was fixed at a height of 1 foot, just above the rim of the test tube. The tube was connected to the input of the Classifier through a silica gel for the intake of aerosol. Silica gel was used to remove the water vapor content. The aerosol flows from the Classifier to the Differential Mobility Analyzer (DMA) and then to the Condensation Particle Counter (CPC). A steady sheath-air flow rate (SFR) was maintained inside DMA to ensure a controlled and stable flow environment. The schematic diagram of the experimental set-up is shown in Fig. 1. The collection of PM emissions for FESEM characterization and EDS analysis was done at the same height and location where the SMPS measurements were done.

After preparation, the nanofuel samples were poured into a 3 mL test tube hung vertically using a clamp holder. The test tube was filled with the fuel sample completely up to the rim in each case to minimize any experimental error. The fuel was ignited using a pilot flame with the help

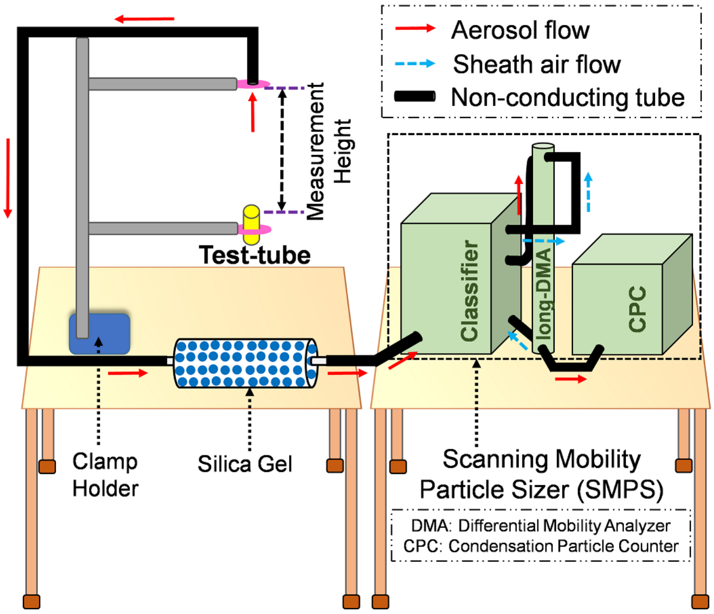


Fig. 1. Schematic diagram of the experimental set-up for PM emissions measurement during flame combustion (strand experiments).

of a gas lighter, which is extinguished as soon as flame combustion takes place above the test-tube rim. The representation of flame for diesel and a few nanofuel samples is shown in Fig. S5.

2.4 Uncertainty Analysis

All the experiments for the measurement of properties, DLS analysis for nanofuel stability, and PM emissions measurement were carried out three times each for better statistical analysis. The study of uncertainty consists of the measurement of standard deviation (σ) for each set of experiments and indicated in the respective plots as error bars. The relative standard deviation (σ_{rel}) aids in understanding the deviation in measured values from the mean value in an effective manner. Table S4 shows the uncertainty analysis in terms of σ_{rel} for various experimental measurements. The uncertainty analysis during DLS measurements is shown in Fig. 2 (Results section 3.1) for a better understanding of the average results. The standard deviation in the measurement of the total number concentration of PM emissions is corroborated in the respective plot (Fig. 5(a)). Similarly, the standard deviation in the measurement of the normalized number concentration of PM emissions at distinct mobility diameter (D_m) is presented separately in Fig. S4 to avoid confusion in the graphical comparison of the number concentration for different test fuel samples.

3 RESULTS AND DISCUSSION

The stability study of nanofuel suspension in terms of dispersibility of the TiO_2 nanoparticles consists of the PSD plots with the intensity of light scattered. The PM emissions investigation during flame combustion includes the comparison of the number concentration with distinct mobility diameter (D_m) in the case of nanofuel samples with diesel. The TNC of UFPs and total PM emissions are analyzed to effectively understand the impact of TiO_2 nano-additives.

3.1 Nanofuel Stability

The gravitational settling of TiO_2 nano-additives depends on their shape, size, and density. Nanoparticles, once dispersed in diesel, tend to aggregate and form large aggregated structures due to various collision mechanisms, including Brownian motion. Thus, the average size of the dispersed particles/aggregated structures will increase, resulting in an increased sedimentation rate of dispersed nanoparticles even though the drag force is also affected. This accelerates the settling of TiO_2 nanoparticles with time, which nullifies the benefits of using nano-additives (Xu, 2018; Zhang, 2014). Therefore, Span80 was used to provide steric stabilization to TiO_2 nanoparticles.

To study the effect of size and morphology on the stability of nanofuel suspension, nanofuel suspension was ball-milled to reduce the size of the dispersed particles. Considering the advantages of mechanical methods in nanoparticle dispersibility, BM and BS were used to reduce the size of the dispersed particles. The PSD analysis presented in Fig. S2 clearly shows the reduction in the

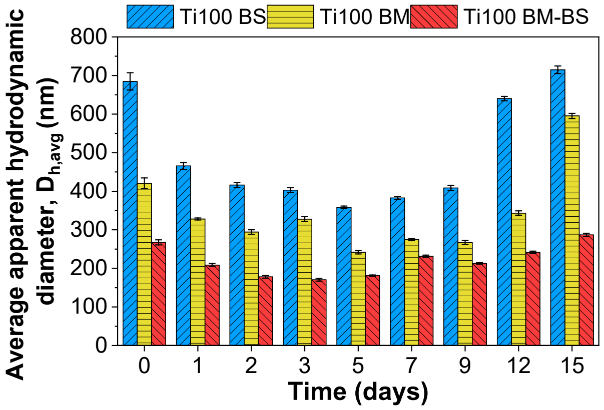


Fig. 2. DLS measurement of the nanofuel samples for 15 days: average apparent hydrodynamic diameter ($D_{h,avg}$) of the TiO_2 nanoparticles dispersed in diesel.

size of the dispersed particles. The long-term stability of nanofuel samples (Ti100 BS, Ti100 BM, Ti100 BM-BS) is studied for 15 days using DLS, and the intensity plots are compared in Fig. S3. The PSD of dispersed TiO_2 nanoparticles in Ti100 BM-BS nanofuel shows the presence of a significant concentration of particles in the submicron- and fine-size range, even after 15 days of nanofuel sample preparation. Fig. 2 shows the average apparent hydrodynamic diameter ($D_{h,avg}$) of the nanoparticles measured up to 15 days. The nanofuel sample, which is ball-milled and bath-sonicated (Ti100 BM-BS), shows the minimum $D_{h,avg}$ and the maximum dispersibility among all the nanofuel samples, clearly demonstrating the positive effects of size reduction of the dispersed particles (Jain *et al.*, 2023).

3.2 Properties of the Test Fuel Samples

The comparison of thermo-physical properties (ρ, CV) of nanofuel with diesel is presented in Table 1. The density of TiO_2 nanoparticles is much higher as compared to neat diesel; therefore, there is a slight increment in the density of nanofuel samples. The blending of nanoparticles into diesel improves the combustion process and heat transfer characteristics of fuel. However, there will be minor effects of the Span80 surfactant on the CV of the fuel. Additionally, the measurement of the CV of different test fuel samples has some experimental errors. Thus, the change in the CV of the fuel is insignificant with the addition of TiO_2 nanoparticles, supporting prior investigations (Örs *et al.*, 2018; Soudagar *et al.*, 2018).

3.3 FESEM Characterization and EDS Analysis

The characterization of PM emitted during the flame combustion of TiO_2-laden nanofuel samples was done using FESEM, as shown in Fig. 3. The EDS analysis shown in Table 2 confirms the evolution of TiO_2 nanoparticles during the flame combustion of nanofuel samples. The evolution of TiO_2 nano-additives affects the number concentration of PM emissions, which is discussed in detail in the further section (Results section 3.4).

3.4 PM Emissions Measurement and Analysis

The PM emissions, including UFPs, were measured using SMPS. Initially, the PM present in ambient air was measured to set the baseline to investigate the effect of nano-additives in PM emissions reduction effectively. The total number concentration (TNC) for ambient air was

Table 1. Properties of the test fuel samples.

Properties	Diesel	Ti100 BS	Ti100 BM-BS	Ti150 BS	Ti150 BM-BS	Ti200 BS	Ti200 BM-BS
Density (ρ, kg m^{-3})	809.8	812.7	813.1	814.2	814.5	815.4	815.7
Calorific value (CV, MJ kg^{-1})	44.542	45.041	45.275	45.510	45.697	45.921	46.089

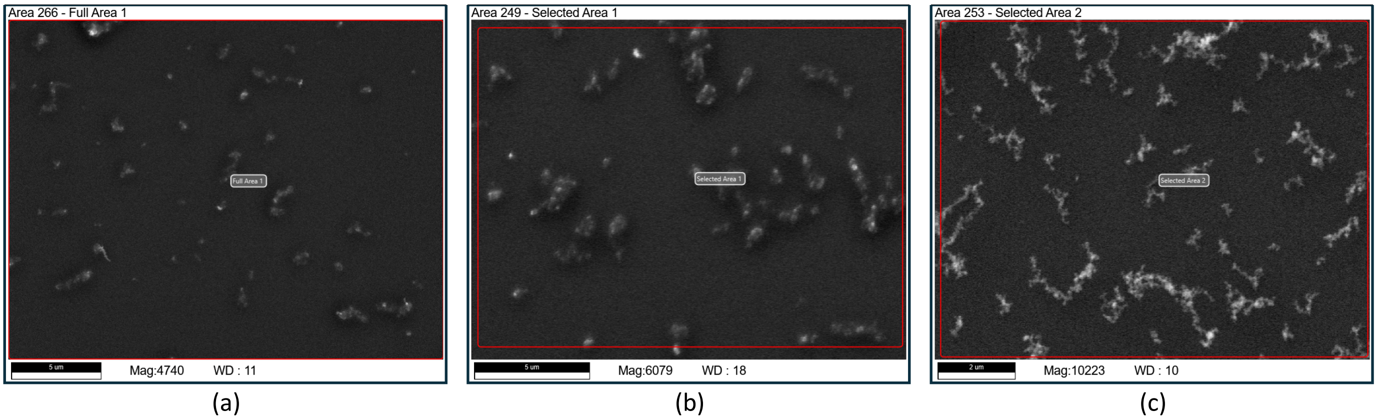


Fig. 3. FESEM images of soot and other PM emissions collected during the flame combustion of the following fuel samples: (a) Neat diesel, (b) Ti100 BM-BS nanofuel, and (c) Ti200 BM-BS nanofuel.

Table 2. Energy-dispersive X-ray spectroscopy (EDS) analysis of PM emissions during flame combustion.

Element	Diesel		Ti100 BM-BS		Ti200 BM-BS	
	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
C K	65.6	71.7	91.1	94.0	60.4	69.1
O K	34.4	28.3	7.1	5.5	34.2	29.3
Ti K	–	–	1.8	0.5	5.4	1.6

5.55 × 10^3 per cm^3. Fig. 4 represents the normalized number concentration ($dN/dlogD_m$) of PM emissions (on a logarithmic scale) at various mobility diameters (D_m) for titania-nanofuel samples (Ti100 BS, Ti100 BM, Ti100 BM-BS, Ti150 BS, Ti150 BM, Ti150 BM-BS, Ti200 BS, Ti200 BM, and Ti200 BM-BS) in contrast to diesel. The PM emissions during the combustion of diesel majorly consist of elemental carbon (i.e., soot) and organic carbon (unburnt fuel, PAH, etc.). The addition of metal oxide additives promotes better oxidation of diesel fuel, and nano-additives, due to the high specific surface area, improve the heat transfer characteristics of the fuel. Consequently, TiO_2 nano-additives improve the combustion characteristics of diesel and aid in the reduction of soot particles (primary and aggregated soot structures) and unburnt hydrocarbon emissions (including PAHs). BM helps in the size reduction of dispersed nanoparticles, so ball-milled nanofuel samples show a better abatement of PM emissions than bath-sonicated samples. Additionally, the nanofuel samples prepared using BM and BS together, shown the maximum stability and size reduction of the dispersed TiO_2 nanoparticles (Fig. 2), leading to the highest reduction in PM emissions.

Figs. 4(a)–4(c) show the variation in PM emissions for the nanofuel samples prepared using distinct methods (i.e., BS, BM, BM+BS) when diesel is blended with 100 ppm/150 ppm/200 ppm TiO_2 nano-additives. Figs. 4(d)–4(f) represent the change in the number concentration of PM emissions when the different quantity of TiO_2 nanoparticles (i.e., 100 ppm, 150 ppm, and 200 ppm) is added to diesel for BS/BM/BM+BS nanofuel samples. Overall, BM-BS nanofuel samples show a better reduction in PM emissions than BS- or BM-nanofuel samples, and 200 ppm TiO_2-nanofuel leads to the maximum reduction in PM emissions. Fig. 5(a) reveals the TNC of PM emissions and the percentage change in TNC when diesel fuel is blended with 100 ppm, 150 ppm, and 200 ppm TiO_2 nano-additives. The results show the reduction in TNC of PM emissions with the use of TiO_2 nano-additives. Moreover, the percentage decrement in TNC depends on the morphology of nano-additives dispersed and the amount of TiO_2 nanoparticles added. The morphology of dispersed nano-additives depends on the preparation method of the nanofuel sample. Fig. 5(b) represents the percentage change in the TNC of PM emissions for the different combinations of nanofuel preparation methods and the amount of TiO_2 nanoparticles added to diesel. The percentage reduction in TNC of the PM emissions increases with the amount of TiO_2 nano-additives for each set of nanofuel samples (BS/BM/BM+BS). However, the percentage decrement in TNC diminishes with the increase in ppm of TiO_2 nano-additives. Similarly, the percentage reduction in TNC is greater for ball-milled nanofuel samples compared to just bath-sonicated nanofuel samples, when the same mass of TiO_2 nano-additive is considered. As discussed in section 3.1, BM aids in the size reduction of TiO_2 nanoparticles dispersed in diesel, and the BM-BS nanofuel sample shows the least $D_{h,avg,}$ and maximum stability with days (Fig. 2). Thus, BM-BS nanofuel samples lead to the largest reduction in PM emissions for 100/150/200 ppm TiO_2-laden diesel fuel. Although there is a reduction in TNC of PM emissions with the addition of TiO_2 nanoparticles for each nanofuel sample (Fig. 5), a similar trend cannot be seen in the case of UFP emissions.

In this study, SFR and AFR are maintained at 3.0 L min^{-1} and 0.3 L min^{-1}, respectively, which fixed the measurement range of D_m from 15.7–637.8 nm. Therefore, to study the effect of nano-additives on ultra-fine particulate emissions, a number concentration of particles within specific D_m ranges were considered. To study the effect of TiO_2 nano-additives on UFPs in detail, the overall size range was divided into four specific ranges:

1) Sub-23 nm region: 15.7–23 nm,
2) Super ultra-fine region: 23–50 nm,
3) Ultra-fine region: 50–100 nm, and
4) Sub-micron region: 100–637.8 nm.

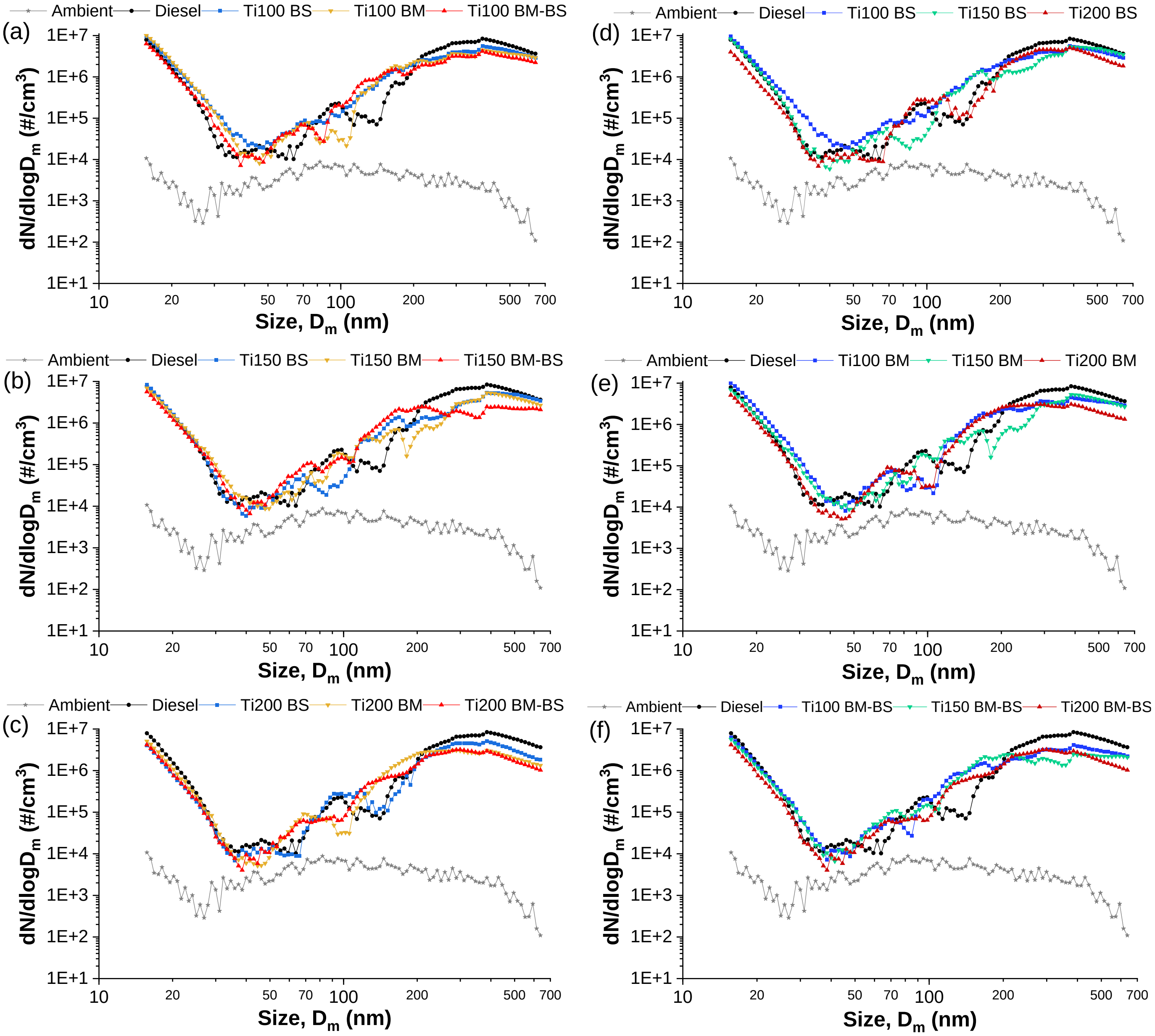
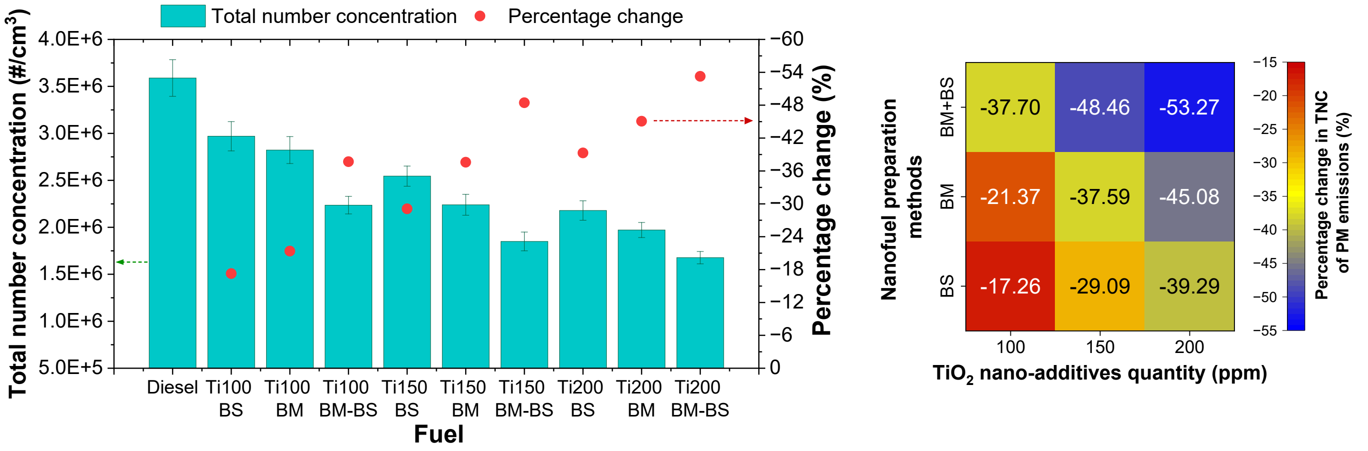


Fig. 4. Measurement of PM emissions with SMPS during the flame combustion of diesel and titania-nanofuel samples: (a)–(c) 100 ppm, 150 ppm, and 200 ppm nanofuel samples, respectively; (d)–(f) bath-sonicated, ball milled, and ball-milled+bath-sonicated nanofuel samples, respectively.

The importance of detailed investigations of UFPs is well-known, considering their impact on human health and the environment (Cassee *et al.*, 2019). The choice of the sub-23 nm range considers the importance of SPN10 (solid particle number > 10 nm) as compared to SPN23 (solid particle number > 23 nm) that is being implemented in Euro-7, European emission standards for vehicles (Samaras *et al.*, 2020). The TNC of PM emissions based on the size range divisions for different fuel samples is shown in Fig. 6. Initial observations show the reduction in TNC for the complete size range of measurement (15.7–637.8 nm); however, on investigating the TNC for D_m < 100 nm, the results show an increment in the TNC of UFPs even after the suppression in organic and elemental carbon due to the addition of metal oxides, for each nanofuel sample. This can be possibly attributed to the emission of TiO_2 nanoparticles during flame combustion, leading to the enhancement in TNC of PM emissions in the sub-23 nm, super ultra-fine, and ultra-fine regions.



(a) (b)

Fig. 5. (a) TNC of PM emissions and the percentage change in TNC for TiO_2-laden nanofuel when compared to diesel, (b) Percentage change in the TNC of PM emissions for distinct nanofuel samples in contrast to diesel.

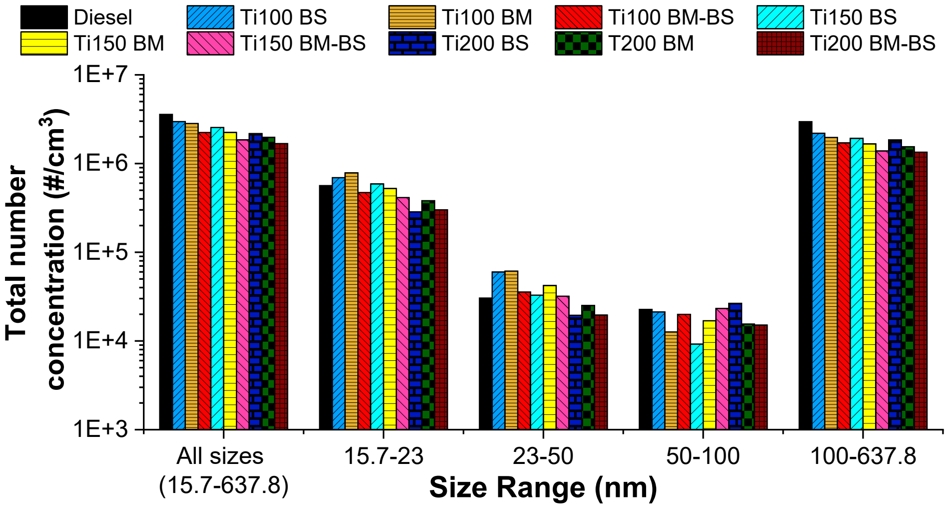


Fig. 6. TNC of PM emissions during flame combustion of diesel and TiO_2-laden diesel fuel samples for distinct size ranges: All sizes (D_m = 15.7–637.8 nm), D_m = 15.7–23 nm, D_m = 23–50 nm, D_m = 50–100, and D_m = 100–637.8 nm.

Although the primary particle size of the TiO_2 nano-additives is relatively small (APS ≤ 25 nm), the size of the aggregated structures of the nanoparticles dispersed in diesel is expected to be significantly larger. Considering this, the size of dispersed nano-additives was modified using bath sonication and ball milling (as discussed in section 3.1). The aggregation of nanoparticles was hindered using Span80 surfactant, and the alteration in size morphology of nanoparticles (or aggregated structures) was achieved using mechanical methods like BM and BS. BM aids in the size modification of the dispersed nanoparticles by grinding them to a lower size, and BS helps in the breakdown of weak aggregates. Thus, for nanofuel samples, despite the suppression in soot and other PM emissions, the evolution of TiO_2 nanoparticles leads to the enhancement in the TNC of UFPs.

Fig. 7 represents the change in the TNC of PM emissions for different combinations of size range and nanofuel samples in contrast to diesel. The analysis shows the reduction in the TNC in the sub-micron region (100–637.8 nm) for all the TiO_2-nanofuel samples. However, the TNC of UFPs increases with the addition of TiO_2 nano-additives, represented by the reddish-yellowish region in Fig. 7. The blue-shade regions depict the reduction in TNC of PM, manifesting the

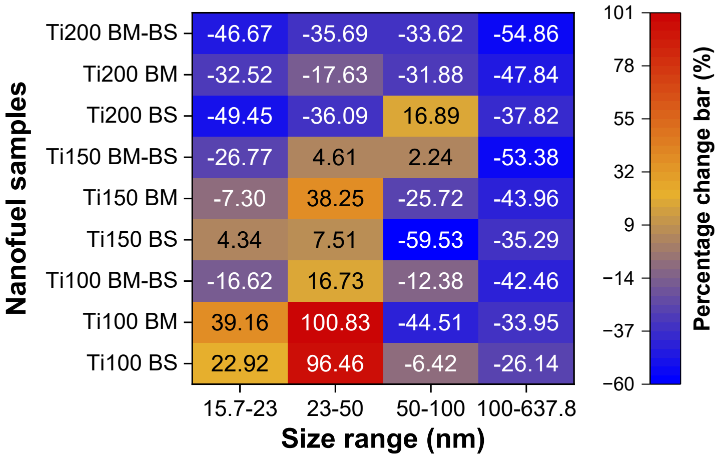


Fig. 7. Percentage change in the TNC of PM emissions during the flame combustion, for distinct size (D_m) range and TiO_2-nanofuel samples in contrast to diesel.

benefits of adding TiO_2 nanoparticles. The percentage increment or decrement in the TNC of PM emissions depends on the size morphology of TiO_2 nanoparticles, the amount of nanoparticles added, and the size range for which the analysis has been made. Thus, for a better analysis of the results, the heat map of the percentage change in TNC has been plotted in Fig. 8 based on two divisions: (I) Figs. 8(a)–8(c), the effect of size modification of nanoparticles for a certain mass of nano-additives, and (II) Figs. 8(d)–8(f), the effect of nano-additives quantity for a specific nanofuel preparation method. In Fig. 8, the red-shade zones represent the percentage enhancement in TNC, and the blue-shade zones represent the percentage reduction in the TNC for nanofuel samples compared to neat diesel.

In Fig. 8(a), the 100 ppm ball-milled sample (Ti100 BM) shows the enhancement in TNC of sub-23 nm (15.7–23 nm) and super ultra-fine (23–50 nm) particles to a greater extent as compared to the 100 ppm bath-sonicated sample (Ti100 BS). Even though the BM aids in the size reduction of dispersed nanoparticles and leads to better suppression of soot and PM emissions, the TiO_2 nanoparticles are themselves evolving during the flame combustion, adding up in the TNC of sub-23 nm and super ultra-fine particles. In the case of the Ti100 BM-BS nanofuel sample, the average size of the dispersed nanoparticles is the smallest (see Fig. 2). Still, there is an enhancement of TNC in the super ultra-fine region and not in sub-23 nm. It does not mean that the nanoparticles are not evolving out in the sub-23 nm region. As nano-additives are beneficial due to high specific surface area, the percentage reduction in soot and other PM emissions occurs to a greater extent for Ti100 BM-BS nanofuel in comparison to Ti100 BS and Ti100 BM nanofuel samples, due to which the cumulative TNC of emissions for sub-23 particles shows optimistic results. Similarly, for the ultra-fine region (50–100 nm) and sub-micron region (100–637.8 nm), the results show the percentage reduction in TNC of PM emissions for 100 ppm TiO_2-nanofuel samples. However, the number concentration of the evolution of nanoparticles will be less than the decrease in the number concentration of PM emissions with the addition of TiO_2 nano-additives, which leads to the net reduction in the TNC. A similar trend can be seen in the case of 150 ppm and 200 ppm nanofuel samples, i.e., Figs. 8(b) and 8(c). The evolution of TiO_2 nanoparticles during flame combustion leads to the increment in TNC, and the regions/zones where the reduction in the TNC of PM emissions dominates will have a net reduction in the TNC. Moreover, one can find that the BM-BS nanofuel sample showed a better reduction in TNC for distinct size ranges and overall PM emissions.

Figs. 8(d)–8(f) represent the percentage change in the TNC of PM emissions with the addition of 100 ppm/150 ppm/200 ppm nano-additives for BS nanofuel, BM nanofuel, and BM-BS nanofuel samples, respectively. The percentage change in TNC has positive values in sub-23 nm and super ultra-fine range for 100 ppm nanofuel sample, depicting that the number concentration of PM emissions increases even after the suppression of soot and PM emissions. The physics behind the enhancement in TNC can be attributed to the evolution of TiO_2 nanoparticles during the flame combustion experiments. Ti100 BM-BS nanofuel sample has the smallest average sized particles

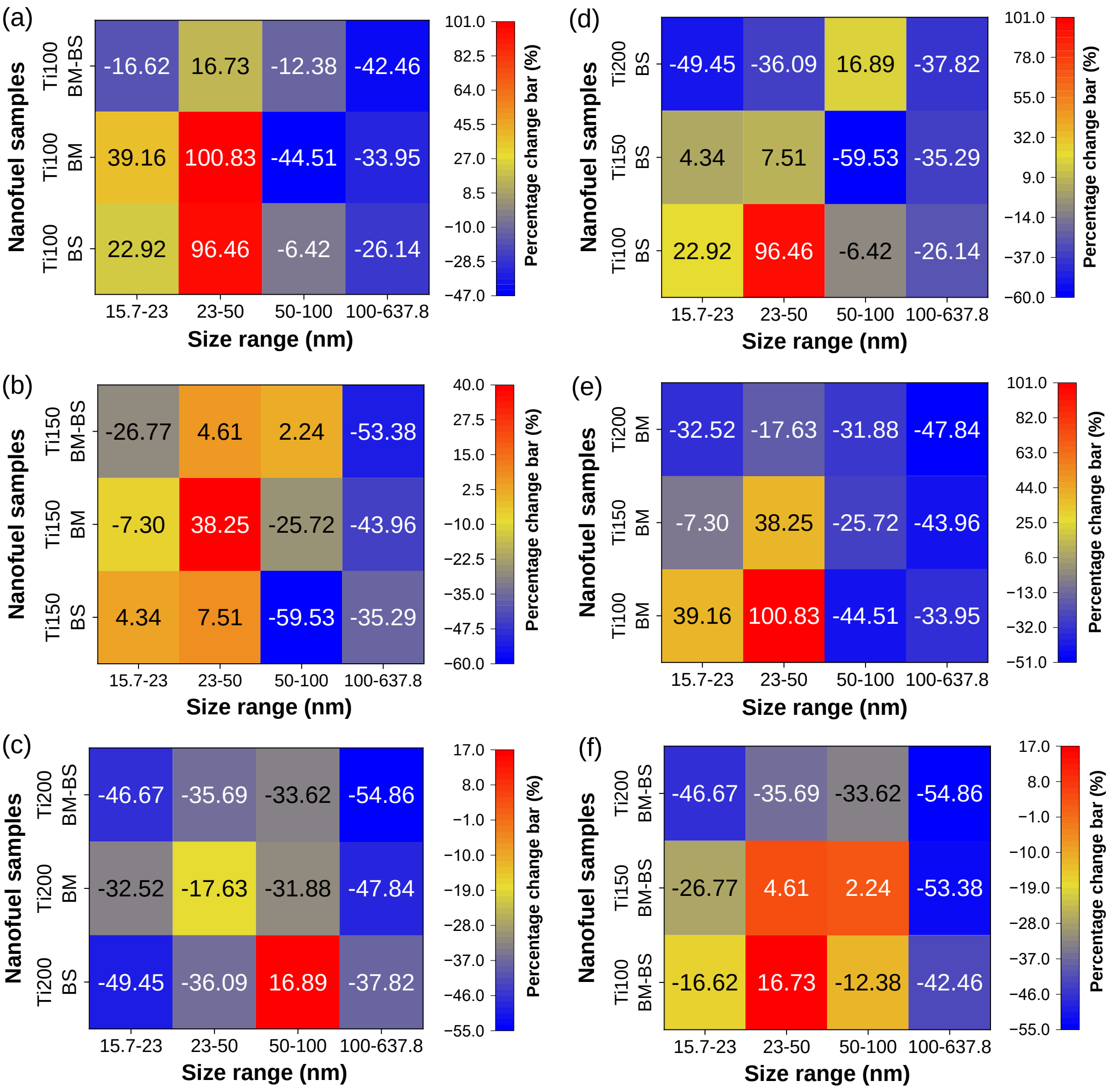


Fig. 8. The percentage change in the TNC of PM emissions with distinct size ranges in comparison to diesel, for the following test fuel samples: (a) 100 ppm TiO_2-nanofuel, (b) 150 ppm TiO_2-nanofuel, (c) 200 ppm TiO_2-nanofuel, (d) BS TiO_2-nanofuel, (e) BM TiO_2-nanofuel, and (f) BM-BS TiO_2-nanofuel.

in the dispersed state, which leads to a maximum reduction in PM emissions. Thus, there is an enhancement in TNC in the super ultra-fine region and a reduction in TNC in the sub-23 nm region. The results also show that the percentage reduction in PM emissions in distinct size ranges increases with the amount of nano-additives. Overall, 200 ppm and BM-BS nanofuel samples showed the highest reduction in TNC of PM emissions. Consequently, the addition of TiO_2 nano-additives to diesel aids in the overall reduction of soot and other PM emissions.

Table 3 compares the current research work with previous studies to underline the significance of modifying the size of the dispersed TiO_2 nanoparticles on nanofuel stability. The prolonged stability of nanofuel suspension demonstrated in this work enhances its practical utility for real-life applications. The advantages of reducing the size of nano-additives on PM emissions can be utilized over a long period. As there is no study specific to diesel/biodiesel flame combustion; therefore, the state-of-the-art comparison for the fine and ultra-fine particulate matter emissions reduction with the addition of TiO_2 nano-additives is not presented here. However, in spite of the variations in the primary size of nanoparticles (APS) and surfactant across studies, the improvement observed in the PM emissions follows a similar trend as that of engine particulate emissions characteristics (Geng *et al.*, 2021).

Table 3. The stability of nanofluid suspension with the addition of TiO_2 nanoparticles.

Authors	Base Fluid/Fuel	Nano-additives (titania)		Nanofuel preparation	Nanofuel stability
		Quantity	Size (APS)		
(Liu *et al.*, 2011)	DI water	20 mg L^{-1}	10 nm	Ultra-sonication for 2 hours	4 days (conc. ratio 4%)
(Leena and Srinivasan, 2015)	Water	500 ppm	15 nm	Ultra-sonication for 3 hours	6 hours
(Venu *et al.*, 2019)	Palm oil-Biodiesel	25 ppm	19–24 nm	Ultra-sonication for 10 min	4 days
(D'Silva *et al.*, 2019)	Diesel	100 mg L^{-1}	$<$ 50 nm	Probe sonication for 30 min	–
(Bello *et al.*, 2020)	Diesel	50 mg L^{-1}	21 nm	Ultra-sonication for 30 min	2 hours
(Vigneswaran *et al.*, 2021)	Diesel-Water	30 ppm	50 ± 5 nm	Stirring 15 min	3 days
Present work	Diesel	100 ppm	$\leq$ 25 nm	Ultra-sonication for 1 hour, Ball milling for 32 min	15 days

4 CONCLUSION

Soot and other PM emissions during the flame combustion of diesel blended with TiO_2 nano-additives have been investigated using SMPS. The study delves into the effect of size modification of dispersed nanoparticles and the amount of TiO_2 nanoparticles on PM emissions. The results show the overall reduction in the number concentration of total PM emissions with an increase in the number concentration of particulates in the specific size ranges. The following are the major findings from the experimental work done to investigate the impact of TiO_2 nanoparticles added to diesel on the emission of PM, including UFPs:

1) The DLS analysis of the nanofuel samples shows that ball milling aids in the size reduction of the dispersed nanoparticles, and the $D_{h,avg}$ is less for BM nanofuel as compared to BS nanofuel, i.e., $D_{h,avg}$ (after 24 hours) is 328.2 nm for Ti100 BM and 465.5 nm for Ti100 BS.
2) Ti100 BM-BS nanofuel sample shows the smallest average sized particles ($D_{h,avg}$ = 208.6 nm, after 24 hours) and the maximum stability in terms of dispersion even after 15 days of nanofuel sample preparation. Thus, ball milling in combination with bath sonication helps in improving the shelf life of the nanofuel.
3) BM is a useful mechanical method that changes the morphology of nanoparticles and aids in improving the combustion phenomenon and reducing PM emissions effectively. There is a reduction of 17.26%, 29.09%, and 39.29% in the TNC for Ti100 BS, Ti150 BS, and Ti200 BS nanofuel samples, respectively, whereas the reduction in the TNC is 21.37%, 37.59%, and 45.08% for Ti100 BM, Ti150 BM, and Ti200 BM nanofuel samples, respectively.
4) BM-BS nanofuel samples showed the maximum reduction in the TNC for a certain mass of TiO_2 nanoparticles added (37.70% for Ti100 BM-BS, 48.46% for Ti150 BM-BS, and 53.27% for Ti200 BM-BS).
5) Nanofuel samples show a reduction in PM emissions; however, the analysis shows an increment in the number concentration of UFPs ($<$ 100 nm). This indicates the evolution of the TiO_2 nanoparticles during flame combustion. The EDS analysis validates the presence of TiO_2 nano-additives evolution in the plume associated with flame combustion.
6) The investigations for 100 ppm- and 150 ppm-nanofuel samples reveal the enhancement in the TNC for the super ultra-fine region (23–50 nm). As BM aids in the size reduction of dispersed nanoparticles, the BM nanofuel samples show more increment in the TNC (100.83% for Ti100 BM, 38.25% for Ti150 BM) as compared to BS nanofuel samples (96.46% for Ti100 BS, 7.51% for Ti150 BS) due to the evolution of nano-additives.
7) In spite of the maximum reduction in the size of dispersed nanoparticles, the BM-BS nanofuel sample showed the least enhancement of TNC in the super ultra-fine region (16.73% for Ti100 BM-BS, 4.61% for Ti150 BM-BS) for a certain amount of nanoparticles added.
8) The TNC in the sub-23 nm region changes (increases or decreases) depending upon the net effect of the evolution of nanoparticles and the suppression of PM emissions for different nanofuel samples.
9) 200 ppm nanofuel samples show a reduction in TNC for almost all size ranges. This does not

invalidate the possibility that nanoparticles are evolving during flame combustion. The cumulative effect of percentage reduction in soot (and other PM emissions) and the evolution of TiO_2 nano-additives shows the net decrement in the TNC.

The experimental investigations reveal that with the addition of TiO_2 nano-additives, there is a reduction in the TNC of total PM emissions during the flame combustion of diesel for the entire size range. However, the detailed analysis of UFPs showed the enhancement in the TNC due to the evolution of TiO_2 nanoparticles. The increment or decrement in the number concentration for distinct size (D_m) depends on the net effect of reduction in PM emissions and evolution of nanoparticles. UFPs play a crucial role in affecting human health and the environment, so the additional burden of nanoparticles in deteriorating air quality needs insight research. Additionally, the measurement of the number concentration of sub-23 nm and UFPs is essential to make the emission norms more stringent. Thus, the detailed investigation of UFPs (1–100 nm) emissions during combustion is essential as the size of primary soot particles lies in the range of a few nanometers. The present study includes the measurement of PM emissions with the help of SMPS using long-DMA that restricts the size range of measurements to 15.7–637.8 nm. Therefore, further studies can be conducted on measuring sub-23 nm and sub-10 nm particles. Additionally, the detailed study of the soot growth mechanism during combustion may help to understand the change in the number concentration of UFPs and submicron particles.

ACKNOWLEDGMENTS

A.J. acknowledges the support of the Ministry of Education through the Prime Minister Research Fellowship (PMRF). The work was partially supported by the Science and Engineering Research Board, India, through the project CRG/2022/0547. The authors gratefully acknowledge the support of Dr. Bidhan Pramanick (Assistant Professor, SES, IIT Goa) and Mr. Adarsh Prakash (Ph.D. Scholar, SMS, IIT Goa) for the FESEM image characterization and EDS. The authors would like to express their gratitude to the Center of Excellence in Colloids, Particulates, and Interfaces (CoE-PCI) at IIT Goa for the use of BS, DLS, EDS, FESEM, and SMPS and the Center of Excellence in Combustion Sciences for the experimental facilities.

SUPPLEMENTARY MATERIAL

Supplementary material for this article can be found in the online version at https://doi.org/10.4209/aaqr.230281

REFERENCES

Ağbulut, Ü. (2022). Understanding the role of nanoparticle size on energy, exergy, thermoeconomic, exergoeconomic, and sustainability analyses of an IC engine: A thermodynamic approach. Fuel Process. Technol. 225, 107060. https://doi.org/10.1016/j.fuproc.2021.107060

Basha, J.S., Al Balushi, M., Soudagar, M.E.M., Safaei, M.R., Mujtaba, M.A., Khan, T.M.Y., Hossain, N., Elfasakhany, A. (2022). Applications of nano-additives in internal combustion engines: a critical review. J. Therm. Anal. Calorim. 147, 9383–9403. https://doi.org/10.1007/s10973-022-11199-6

Bello, Y.H., Ookawara, S.A., Ahmed, M.A., El-Khouly, M.A., Elmehasseb, I.M., El-Shafai, N.M., Elwardany, A.E. (2020). Investigating the engine performance, emissions and soot characteristics of CI engine fueled with diesel fuel loaded with graphene oxide-titanium dioxide nanocomposites. Fuel 269, 117436. https://doi.org/10.1016/j.fuel.2020.117436

Ben Said, L., Kolsi, L., Ghachem, K., Almeshaal, M., Maatki, C. (2022). Advancement of nanofluids in automotive applications during the last few years—a comprehensive review. J. Therm. Anal. Calorim. 147, 7603–7630. https://doi.org/10.1007/s10973-021-11088-4

Canteenwalla, P., Thomson, K., Smallwood, G., Johnson, M. (2007). Soot emissions from turblent diffusion flames burning simple alkane fuels, Presented at the Combustion Institute Canadian

Section, 2007 Spring Technical Meeting [Proceedings], NRC Publications Archive. https://nrc-publications.canada.ca/eng/view/accepted/?id=b1e124bf-252c-4d0b-b945-a542320351ee

Cassee, F.R, Morawska, L., Peters, A., Künzli, N., Wierzbicka, A., Buonanno, G., Cyrys, J., SchnelleKreis, J., Kowalski, M., Riediker, M., Birmili, W., Querol, X., Yildirim, A., Elder, A., Yu, I., Øvrevik, J., Hougaard, K., Loft, S., Schmid, O., Schwarze, P., *et al.* (2019). White Paper: Ambient Ultrafine Particles: Evidence for Policy Makers. https://efca.net/files/WHITE%20PAPER-UFP%20evidence%20for%20policy%20makers%20(25%20OCT).pdf

Chinnasamy, C., Tamilselvam, P., Ranjith, R. (2019). Influence of aluminum oxide nanoparticle with different particle sizes on the working attributes of diesel engine fueled with blends of diesel and waste plastic oil. Environ. Sci. Pollut. Res. 26, 29962–29977. https://doi.org/10.1007/s11356-019-06139-1

Cotton, D.H., Friswell, N.J., Jenkins, D.R. (1971). The suppression of soot emission from flames by metal additives. Combust. Flame 17, 87–98. https://doi.org/10.1016/S0010-2180(71)80142-6

D'Silva, R., Fernandes, N., Menezes, M., D'Souza, P., Pinto, V., Kaliveer, V., Gopalakrishna, B.K., Bhat, T. (2019). Effect of TiO_2 nanoparticle concentration in Pongamia Pinnata methyl ester on performance and emission characteristics of CI engine. AIP Conf. Proc. 2080, 030006. https://doi.org/10.1063/1.5092909

Dinesha, P., Kumar, S., Rosen, M.A. (2021). Effects of particle size of cerium oxide nanoparticles on the combustion behavior and exhaust emissions of a diesel engine powered by biodiesel/diesel blend. Biofuel Res. J. 8, 1374–1383. https://doi.org/10.18331/BRJ2021.8.2.3

Dobrzyńska, E., Szewczyńska, M., Puchałka, B., Szczotka, A., Woodburn, J. (2022). The effect of nano-additives on diesel engine exhaust emissions. Polish J. Environ. Stud. 31, 25–33. https://doi.org/10.15244/pjoes/138209

Gad, M.S., Ağbulut, Ü., Afzal, A., Panchal, H., Jayaraj, S., Qasem, N.A.A., El-Shafay, A.S. (2023). A comprehensive review on the usage of the nano-sized particles along with diesel/biofuel blends and their impacts on engine behaviors. Fuel 339, 127364. https://doi.org/10.1016/j.fuel.2022.127364

Gaffney, J.S., Marley, N.A. (2009). The impacts of combustion emissions on air quality and climate – From coal to biofuels and beyond. Atmos. Environ. 43, 23–36. https://doi.org/10.1016/j.atmosenv.2008.09.016

Geng, L., Li, S., Xiao, Y., Chen, H., Chen, X., Ma, Y. (2021). Influence of the addition of titanium oxide nanoparticles to Fischer-Tropsch diesel synthesised from coal on the combustion characteristics and particulate emission of a diesel engine. Process Saf. Environ. Prot. 145, 411–424. https://doi.org/10.1016/j.psep.2020.11.030

Health Effects Institute (HEI) (2013). Understanding the Health Effects of Ambient Ultrafine Particles. Health effect Institute, Boston, MA (Vol. 3, Issue 1). https://www.healtheffects.org/publication/understanding-health-effects-ambient-ultrafine-particles

Hirasawa, T., Sung, C.J., Yang, Z., Joshi, A., Wang, H. (2004). Effect of ferrocene addition on sooting limits in laminar premixed ethylene-oxygen-argon flames. Combust. Flame 139, 288–299. https://doi.org/10.1016/j.combustflame.2004.09.002

Hu, C., Li, W., Lin, Q., Cheng, X., Huang, Q., Zhang, H., Wang, Z. (2016). Effects of ferrocene on flame temperature, formation of soot particles and growth of polycyclic aromatic hydrocarbons. J. Energy Inst. 90, 893–901. https://doi.org/10.1016/j.joei.2016.08.005

Jain, A., Ambekar, A., Thajudeen, T. (2023). Experimental investigation on the effect of size modification of Alumina nano-additives on the performance and emission characteristics of a compression ignition engine. J. Therm. Anal. Calorim. 149, 479–494. https://doi.org/10.1007/s10973-023-12684-2

Jeon, S., Thajudeen, T., Hogan, C.J. (2015). Evaluation of nanoparticle aggregate morphology during wet milling. Powder Technol. 272, 75–84. https://doi.org/10.1016/j.powtec.2014.11.039

Kegl, T., Kovač Kralj, A., Kegl, B., Kegl, M. (2021). Nanomaterials as fuel additives in diesel engines: A review of current state, opportunities, and challenges. Prog. Energy Combust. Sci. 83, 100897. https://doi.org/10.1016/j.pecs.2020.100897

Leena, M., Srinivasan, S. (2015). Synthesis and ultrasonic investigations of titanium oxide nanofluids. J. Mol. Liq. 206, 103–109. https://doi.org/10.1016/j.molliq.2015.02.001

Liu, X., Chen, G., Su, C. (2011). Effects of material properties on sedimentation and aggregation of titanium dioxide nanoparticles of anatase and rutile in the aqueous phase. J. Colloid Interface Sci. 363, 84–91. https://doi.org/10.1016/j.jcis.2011.06.085

Liu, X., Kong, S., Yan, Q., Liu, H., Wang, W., Chen, K., Yin, Y., Zheng, H., Wu, J., Qin, S., Liu, J., Feng, Y., Yan, Y., Liu, D., Zhao, D., Qi, S. (2020). Size-segregated carbonaceous aerosols emission from typical vehicles and potential depositions in the human respiratory system. Environ. Pollut. 264, 114705. https://doi.org/10.1016/j.envpol.2020.114705

Maciejczyk, P., Chen, L.C., Thurston, G. (2021). The role of fossil fuel combustion metals in $PM_{2.5}$ air pollution health associations. Atmosphere 12, 1–34. https://doi.org/10.3390/atmos12091086

Matti Maricq, M. (2012). Soot formation in ethanol/gasoline fuel blend diffusion flames. Combust. Flame 159, 170–180. https://doi.org/10.1016/j.combustflame.2011.07.010

McCown, K.W., Demko, A.R., Petersen, E.L. (2014). Experimental techniques to study linear burning rates of heterogeneous liquid monopropellants. J. Propuls. Power 30, 1027–1037. https://doi.org/10.2514/1.B35093

Mehrizi, A.A., Karimi-maleh, H., Naddafi, M., Karaman, O., Karimi, F., Karaman, C., Cheng, C.K. (2022). Evaporation characteristics of nanofuel droplets: A review. Fuel 319, 123731. https://doi.org/10.1016/j.fuel.2022.123731

Örs, I., Sarıkoç, S., Atabani, A. E., Ünalan, S., Akansu, S.O. (2018). The effects on performance, combustion and emission characteristics of DICI engine fuelled with TiO_2 nanoparticles addition in diesel/biodiesel/n-butanol blends. Fuel 234, 177–188. https://doi.org/10.1016/j.fuel.2018.07.024

Rashid, M.M., Forte Tavčer, P., Tomšič, B. (2021). Influence of titanium dioxide nanoparticles on human health and the environment. Nanomaterials 11, 2354. https://doi.org/10.3390/nano11092354

Samaras, Z.C., Andersson, J., Bergmann, A., Hausberger, S., Toumasatos, Z., Keskinen, J., Haisch, C., Kontses, A., Ntziachristos, L.D., Landl, L., Mamakos, A., Bainschab, M. (2020). Measuring automotive exhaust particles down to 10 nm. SAE Int. J. Adv. Curr. Pract. Mobility 3, 539–550. https://doi.org/10.4271/2020-01-2209

Sezer, İ. (2019). Effect of nano materials additives on fuel properties and combustion characteristics. J. Fac. Eng. Archit. Gazi Univ. 34, 115–136. https://doi.org/10.17341/gazimmfd.416469

Sher, E. (1998). Handbook of Air Pollution from Internal Combustion Engines: Pollutant Formation and Control. Academic Press, London. https://doi.org/10.1016/B978-0-12-639855-7.X5038-8

Sonwani, S., Madaan, S., Arora, J., Suryanarayan, S., Rangra, D., Mongia, N., Vats, T., Saxena, P. (2021). Inhalation exposure to atmospheric nanoparticles and its associated impacts on human health: a review. Front. Sustain. Cities 3, 690444. https://doi.org/10.3389/frsc.2021.690444

Soudagar, M.E.M., Nik-Ghazali, N.-N., Abul Kalam, Md., Badruddin, I.A., Banapurmath, N.R., Akram, N. (2018). The effect of nano-additives in diesel-biodiesel fuel blends: A comprehensive review on stability, engine performance and emission characteristics. Energy Convers. Manage. 178, 146–177. https://doi.org/10.1016/j.enconman.2018.10.019

Tomar, M., Kumar, N. (2019). Influence of nanoadditives on the performance and emission characteristics of a CI engine fuelled with diesel, biodiesel, and blends–a review. Energy Sources Part A 42, 2944–2961. https://doi.org/10.1080/15567036.2019.1623347

Vardoulakis, S., Giagloglou, E., Steinle, S., Davis, A., Sleeuwenhoek, A., Galea, K.S., Dixon, K., Crawford, J.O. (2020). Indoor exposure to selected air pollutants in the home environment: a systematic review. IJERPH 17, 8972. https://doi.org/10.3390/ijerph17238972

Venu, H., Subramani, L., Raju, V.D. (2019). Emission reduction in a DI diesel engine using exhaust gas recirculation (EGR) of palm biodiesel blended with TiO_2 nano additives. Renew. Energy 140, 245–263. https://doi.org/10.1016/j.renene.2019.03.078

Vigneswaran, R., Balasubramanian, D., Sastha, B.D.S. (2021). Performance, emission and combustion characteristics of unmodified diesel engine with titanium dioxide (TiO_2) nano particle along with water-in-diesel emulsion fuel. Fuel 285, 119115. https://doi.org/10.1016/j.fuel.2020.119115

Walsh, M.P. (2014). $PM_{2.5}$: global progress in controlling the motor vehicle contribution. Front. Environ. Sci. Eng. 8, 1–17. https://doi.org/10.1007/s11783-014-0634-4

World Health Organization (WHO) (2018). World health statistics 2018: monitoring health for the SDGs, sustainable development goals. World Health Organization, Geneva.

Xu, F. (2018). Review of analytical studies on TiO_2 nanoparticles and particle aggregation, coagulation, flocculation, sedimentation, stabilization. Chemosphere 212, 662–677. https://doi.org/10.1016/j.chemosphere.2018.08.108

Zhang, W. (2014). Nanoparticle aggregation: Principles and modeling. Adv. Exp. Med. Biol. 811, 20–43. https://doi.org/10.1007/978-94-017-8739-0_2

Zhou, Y., Hou, D., You, X. (2023). Effects of iron addition on the collision of polycyclic aromatic hydrocarbon clusters: a molecular dynamics study. J. Phys. Chem. A 127, 1026–1035. https://doi.org/10.1021/acs.jpca.2c06666