Performance and exhaust emissions in a diesel engine fuelled with a blend including ZnO nanoparticles and nano-emulsions

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Abstract. A realisation of the need to curtail consumption of fossil fuels with high atmospheric emissions has led researchers to investigate alternatives in recent years. Nano-emulsions (NE) with water suspended at nano-size inside diesel fuel offer better air/fuel blends during the combustion process, creating fuels with higher combustion efficiency and lower emissions. For this study, a nano-emulsion with 12 W% was prepared in a high-speed homogenizer to produce an NE fuel with 26 nm effective droplet diameter, based on optimisation calculations in Design-Expert software. Three doses of zinc oxide (50, 100, and 150 ppm) with average diameters 10 to 30 nm were mixed into prepared nano-emulsion samples. Five fuel blends, Diesel, NE, NE+50 ppm ZnO, NE+100 ppm ZnO, and NE+150 ppm ZnO were then examined for performance and emissions in a four-cylinder Fiat Diesel engine at 1,500 rpm constant speed and 400 bar fuel injection pressure, with a changing operating load. Brake specific fuel consumption (BSFC) was reduced by 16.4% with an increase of 10.2% in thermal efficiency for NE+150 ppm ZnO in comparison with the neat diesel at higher loads of 352.88 kN/m 2 . CO, NOx, HC, and smoke opacity were also reduced by 18%, 13.2%, 17.1%, and 32.8%, respectively for NE+150 ppm ZnO. This research thus offer direction for the utilisation of ZnO nanoparticles in the reduction of exhaust emissions and fuel consumption, offering both economic and environmental benefits.

Keywords: zinc oxide nanoparticles, nano-emulsions, exhaust emissions, engine performance, micro-explosions

1. Introduction
Continuing growth in internal combustion engine use has resulted in ongoing increases in fuel demands [1]. Petrol and diesel are the two main fuels used in internal combustion engines, both of which are derived from crude oil. While diesel engines provide better thermal efficiency and fuel economy, this is accompanied by high levels of emissions and pollution such as CO, HC, PM, and NOx due to incomplete combustion inside the combustion chamber [2]. This problem has become critical due to a realisation of the resulting damage to human health, such as breathing problems and heart disease, as well as the ongoing damage to the climate and environmental hazards such as acid rain and the formation of ozone at ground level.

Adding water to diesel in the form of a nano-emulsion is one of the strategies used to ensure more complete combustion of diesel fuel inside combustion cylinders [3,4]. Water droplets are vapourised due to having higher volatility than pure diesel, and the resulting micro-explosions spread the diesel fuel more evenly [5]. The positive impacts of water content at the nano-metre size include better fuel/air...
blending from the improved diffusion of diesel-bound water droplets [6]. Chaitanya et al. [27] experimentally investigated the impact of water/diesel emulsions prepared by different surfactants; their results confirmed that NOx emissions were reduced up to 38% with both Span20 and Tween20 surfactants and 2% water content. Ithnin et al. [28] also performed an experimental study of a water in diesel emulsion that showed PM and NOx emissions being reduced, although they noted that CO2 emissions were slightly higher.

The size of droplets has the greatest specific impact in the reduction of NOx formation. Lin and Tsai [26] studied the characteristics of diesel engine emissions using fuels with solketal droplets, and thus confirmed that a nano-emulsion had lower NOx, and higher CO2 emissions than a micro-emulsion. Peak flame temperature also significantly decreases in the presence of nano-size water droplets, contributing to the decrease in NOX emissions noted, as shown by many investigators [24]. Mohankumara and Senthilkumarb [23] noted further that PM formation decreased with any enhancement of air-fuel mixing that resulted in more complete oxidation of fuel. Nano-metal oxides with high energy density thus offer several further benefits by enhancing fuel oxidation and shortening ignition delay due to catalytic effect. Beloni et al. studied the combustion characteristics of liquid hydrocarbon fuel with metal-based fuel additives, concluding that fuel blends with NPs have higher ignition rates than diesel fuels without NPs [7].

Nanomaterials have higher activity and act more effectively than bulk materials due to the increase in surface area to volume ratio. The catalytic effect and size of specific nanomaterials are thus a basis of choice for improvements to the combustion process [8]. Various type of nanomaterials, such as cerium oxide, iron oxide, and copper oxide have been investigated as fuel additives by researchers [9], though all tend to show lower emissions and higher performance than fuel without any NP.

Abhishek et al. investigated the impact of ZnO nanoparticles in a four-stroke multi cylinder engine, concluding that ZnO’s very high surface area to volume ratio makes it particularly useful for combustion studies, further supported by its capability to act as an oxygen buffer, causing simultaneous oxidation of CO and HC, reducing nitrogen and sulphur oxides, and thus significantly reducing emissions and fuel increasing the efficiency of combustion [19].

Venkatesan and Kadiresh [10] used three levels (500, 750, and 1,000 mg) of ZnO NP per litre of diesel, mixed with an ultrasonic shaker. A diesel engine was then run at 1,500 rpm with a compression ratio of 17.5:1 and a brake power output of 4.4 kW. The flash point, fire point, and calorific value were all increased by the increase in the ZnO NP level, while reductions in BSFC and improvement in BTE were also noted. Engine emissions (HC, NOx, CO, and smoke) were reduced for the 1,000 mg ZnO NP dosage at maximum power output.

Kamesh and Madhu [31] compared the effects of three mixed oxides, Al2O3, Fe2O3, and ZnO, in pure diesel using an ultrasonic probe. A single-cylinder Kirloskar AV1 water-cooled DI diesel engine was used to study the effects of the nanoparticles, and ZnO was found to effectively reduce the CO emissions, by up to 40% and the HC emissions by 38.81%, though a 6.98% increase in CO2 emissions at 180 bars was also observed.

Karthikeyan et al. [11] used ZnO nanoparticles mixed in Pomolion Stearin wax oil in a single-cylinder direct injection diesel engine. The ZnO additive was dispersed at 50 and 100 ppm, with particles less than 100 nm in diameter, producing lower fuel consumption due to higher calorific value and higher BTE. With regard to emissions, of CO, HC, and smoke opacity was increased, while NOx emissions showed no significant difference.

Hamadi et al. [12] investigated the effect of concentrations of 50 and 100 ppm ZnO, blended ultrasonically in diesel fuel, used in a four-cylinder, water-cooled, naturally aspirated Fiat diesel engine. The fuel blend test was done at a constant speed 1,500 rpm at 400 bars injection pressure with varying operating loads on the engine. Lower production of HC and CO emissions were found at higher loads, while low loads showed an increase. BSFC was reduced and BTE was higher than for pure diesel.

Ashley et al. [29] studied the impact of three fuels, diesel, biodiesel (derived from waste cooking oil), and biodiesel fuel with 80 ppm ZnO NP, in a TV2 diesel engine. They obtained a 4% increase in BTE and a reduction of about 9% in BSFC. The emissions of CO and unburnt hydrocarbons were reduced by
25% and 14% of NOx, respectively. A significant reduction of 30% in CO emissions was also noted in the presence of fuel containing zinc oxide nanoparticles. Selvaganapthy et al. [30] experimentally investigated diesel fuel as compared to diesel containing two levels (250, 500) of ZnO NP with average particle size 24 to 71 nm in a four-stroke single cylinder diesel engine. A magnetic stirrer was used for blending the nanoparticles in diesel fuel. This resulted in a reduction in ignition delay and an increase in BTE, while NOx emissions increased.

The main aim of the current investigation is to study the effect of ZnO nanoparticles added in three doses to diesel create NE fuels by means of high-speed homogenisation on diesel engines, including the effects on both performance and exhaust emissions. In this work, the nano-emulsions were prepared according to the optimum conditions generated using appropriate design software (Design Expert); thus, the NE fuels were blended three-level doses of ZnO in order to study performance and exhaust emission differences between the blended fuels and neat diesel experimentally.

2. Material and methods

Conventional diesel fuel was provided by the local Dura Refinery (Baghdad -Iraq) to be used as the continuous phase of the NE fuels. Two surfactants, supplied by CDH Co. India, were used to stabilise the emulsions. The preparation of the fuel and additives are explained in the following section.

2.1. Preparation of NE Fuel

The NE fuel sample was prepared using the high energy method (High energy homogenizer speed-rotator-stator Heidolph DIAx 900). The six key variables are tabulated in table 1, including the specific limits offered for optimisation by the Design Expert software used to plan the preparation of NE fuels. Fifty-four trials are utilised in a central composite design to determine the optimum value for each factor. Full information about this optimisation process is presented in Khidhir and Hamadi [25].

| Table 1. Factors in central composite design. |
|---------------------------------------------|
| Factors                  | Initial value | End value | Optimum value |
| Water content %          | 0             | 10        | 30            |
| Emulsifier %             | 1             | 5         | 5             |
| rpm                      | 5000          | 25000     | 15000         |
| Time of mixing(min)      | 10            | 50        | 30            |
| pH                       | 7             | 14        | 10.5          |
| HLB                      | 4.5           | 6.5       | 6             |

Two surfactants, Polyoxyethylene Sorbitan monooleate (Tween80) and Sorbitan monooleate (Span80) were mixed according to Eq. 1 to make the required HLB.

\[ \%(T) = \frac{100 \times (X - HLB_{(S)})}{[HLB_{(T)} - HLB_{(S)}]} \]  \[ (1) \]

\[ \%(S) = 100 - \%(T) \]

X= Required HLB
T = Tween 80
S = Span 80
Figure 1. Chemical structures of surfactants.

The prepared HLB was then added to neat diesel and a stirring speed of 5,000 rpm applied for 10 minutes. Water was added to the mixture of emulsifiers and diesel and mixed according to the optimised conditions. The average diameter for the water droplets was 26 nm, as measured by Dynamic light scattering techniques (DLS, Brookhaven 90 Plus, USA) at 25 °C.

2.2. Nanoparticle blending

Zinc oxide in nano-particle size, with average diameter 10 to 30 nm, as manufactured by SDS Co. USA, was used. After preparation of NE to the required specifications according to the optimum conditions, three-level doses of ZnO NP were blended into the NE and mixed for 10 minutes at 15,000 rpm in the homogeniser, which is a standard dispersion method for nanoparticles. The ZnO NP specifications are tabulated in table 2.

Table 2. Specifications of ZnO nanoparticles

| Specification       | Value                  |
|---------------------|------------------------|
| Purity:             | 99+%                   |
| APS:                | 10-30 nm               |
| Colour:             | White                  |
| Crystal Phase:      | single crystal         |
| Morphology:         | nearly spherical        |
| SSA:                | 20-60 m²/g             |
| True Density:       | 5.606 g/cm³            |

3. Engine Setup

A four-stroke TD 313 diesel engine was used to study the emission and performance characteristics of the prepared diesel, NE, and NE+ZnO fuel blends with different loads with the help of a closed-loop controller. The test engine was coupled with an eddy current dynamometer to provide the brake load, and the fuel consumption in the engine was determined the time used to consume 200 ccs of each fuel sample, as delivered by burette, with the time recorded using a stopwatch. A photograph of the diesel engine used is shown in figure 2. The concentrations of five gases, unburned hydrocarbons, CO, CO₂, O₂, and NOₓ, were measured using an automotive emissions analyser model HG-550, provided by EGMA.

To measure oxygen and nitrogen oxide emissions, an electrochemical technique was used, while for the rest of the gases, a non-dispersive infrared (NDIR) measuring method was applied. Smoke emissions from the combustion of fuels were measured using an AVL-415 smoke meter. The filter smoke number (FSN) is the measuring unit used in smoke meters; this is based on thermo-desorption and particle counts on filter paper. The fuels were added individually to the fuel tank in a minimum 2 litre quantity in each test, then allowed to reach the valves on the fuel supply line. After that, the engine was run for three minutes to stabilise before any measurements were taken in each case.
The gas analyser and smoke metre were then activated for emission measurement, and readings of unburned hydrocarbons, carbon monoxide, nitrogen oxides and smoke opacity were taken with the help of a flue gas analyser and smoke meter. This procedure was repeated for several different loads for each fuel, though the rpm was kept constant by using a screw arrangement. All data were recorded before the engine was stopped and drained to allow the process to be repeated for the next fuel type. Specifications of the diesel engine are tabulated in table 3.

Table 3. Technical specifications of the experimental engine

| Specification                      | Value                                |
|-----------------------------------|--------------------------------------|
| Engine type                       | 4 cylinder, 4-stroke                  |
| Engine model                      | TD 313 Diesel engine reg              |
| Combustion type                    | DI, water-cooled, natural aspirated  |
| Displacement                      | 3.666 L                              |
| Valve per cylinder                | Two                                  |
| Bore                              | 100 mm                               |
| Stroke                            | 110 mm                               |
| Compression ratio                 | 17                                   |
| Fuel injection pump               | Unit pump 26 mm diameter plunger     |
| Fuel injection nozzle             | Nozzle hole diameter. (0.48mm), Spray angle= 160o, Nozzle opening pressure= 40 Mpa |

4. Results and discussion
The current study goal was to investigate the effect of fuel type (pure diesel, NE, and three levels of ZnO in NE) on the performance of a diesel engine with regard to combustion emissions at different engine loads and a constant speed. All fuel blends were thus tested under the same conditions and experiment time to obtain comparative results to permit a study of the effects of NPs.
4.1. Fuel properties

**Table 4.** Comparison Between Diesel Fuel and Prepared NE Fuel

| Properties (measured) | Diesel fuel | NE fuel |
|-----------------------|-------------|---------|
| Calorific value (kJ/kg) | 44800       | 38850   |
| Flash point (°C)      | 54          | 61      |
| Viscosity at 40 °C (cSt) | 3.268      | 4.56    |
| Density (g/cm³)       | 0.87        | 0.882   |

The optimised fuel as prepared had a 38,850 kJ/kg calorific value, lower than that of the net fuel which had 44,800 kJ/kg due to the presence of water in the former. The higher flashpoint of NE fuel (61 °C) indicates that the volatility of diesel fuel is increased in the presence of water droplets. The viscosity of NE fuel was recorded as 4.56 cSt, higher than the net fuel, and a higher density was also found in the NE fuel (0.882 g/cm³), as shown in Table 4.

4.2. Performance characteristics

Brake specific fuel consumption (BSFC) and brake thermal efficiency (BTE) are two parameters that determine the performance of an engine. For all fuel blends, enhancement was observed in terms of a reduction in BSFC and an increase in BTE as compared to pure diesel fuel.

4.2.1. Brake Specific Fuel Consumption.

Analysis of BSFC was done for all five fuels (Diesel, NE, NE+50 ppm ZnO, NE+100 ppm ZnO, and NE+150 ppm ZnO) at a constant speed of 1,500 rpm. The compression ratio was set to a constant value 17, while the load on the engine varied from 5 to 15 kg in a step-change of 2.5 kg. Figure 3 shows that BSFC decreased with the increase in engine load for all fuel blends due to the higher percentage increase in brake power with load as compared to the increase in fuel consumption. This result corresponds with Karthikeyan et al. [11], who that used ZnO NP at a 1,500-rpm constant speed and found the as the level of dose increased from 50 to 100 ppm, BSFC increased.

NE fuel has a higher BSFC due to the partial replacement of diesel fuel by water, which reduces the brake power by fuel due to lower heat content. This leads to a higher consumption of fuel being required to supply the same brake power at the same load.

The presence of ZnO NP helps promote combustion activity due to catalytic action, however, creating enhancement in combustion at high temperatures. The high surface to volume ratio of nanoparticles provides better atomisation of fuel blends at high temperatures [13, 14, 19], and thus, increasing the level of ZnO from 50 to 150 ppm in NE fuel led to a reduction in BSFC with increases in the load. A higher BSFC was thus obtained by NE+150 ZnO; however, the difference in terms of decreasing fuel consumption was seen only in a narrow range despite increasing the dose by 50 ppm at each step.
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Figure 3. Variation of BSFC with Load (bmep) kN/m².

4.2.2. Brake thermal efficiency.

As shown in Figure 4, BTE increases with an increase of the load on the engine in all fuel blends, due to the higher temperature created by increasing the load, which increases fuel consumption. ZnO NP doped fuel has a greater calorific value than pure fuel [12], offering greater brake power and better BTE. The ZnO catalyst also oxidises the fuel more efficiently and reduces fuel evaporation time, leading to complete fuel burning and increased efficiency, increasing BTE [10].

Figure 4. Variation of BTE with Load (bmep) kN/m².

4.3. Emission characteristics

Various emissions, including unburnt hydrocarbons (HC), carbon monoxide, carbon dioxide and nitrogen oxides (NOx), are emitted from a diesel engine during the combustion process. Carbon monoxide gas is emitted where there is a lack of oxygen, while NOx gases are produced when the temperature range reaches 2,500 to 3,000 K inside the cylinder of the engine and there is an excess of oxygen.

Reducing the emissions of these gases required a special control strategy, as attempting to decrease one such gas may cause another gas to become more concentrated and lead to worse environmental emissions. An example of this would be providing oxygen into the cylinder so that all CO gas is
converted to CO\textsubscript{2}; however, this would increase the emission of NO\textsubscript{x}; reducing the temperature in the combustion cylinder to try to address this would then increase HC and smoke emissions.

4.3.1. Carbon monoxide.
The variation of CO emission observed across this experimental work is illustrated in Figure 5 for all fuel blends. Increasing the load on the engine leads to a decrease in CO emissions in all fuel mixtures. Pure diesel fuel shows the lowest CO emissions at the start point, as net diesel at low load does not contain any water droplets, causing the hydrocarbons in the fuel to burn more easily at that pressure and temperature. The NE fuel shows higher CO emissions at low loads due to the presence of water droplets in the cylinder, which act as an obstacle to the combustion process by quenching flames until the cylinder warms up. The water present in the NE fuel sample is also responsible for the increase in ignition delay period due to its high latent heat of vaporisation, which causes additional fuel accumulation in the combustion cylinder during the delay period. The catalytic effect of nanoparticles, however, leads to a higher cetane number and shorter delay period, facilitating more complete combustion [15,16]. Nevertheless, this phenomenon disappears with the increase in the load and as temperatures increase, as shown in Figure 5. Better fuel/air blending is obtained by the atomisation of fine water droplets in NE fuel as a result of the secondary explosions, which facilitates more complete combustion. Fuel NE+100 ZnO and NE+150 ZnO show lower CO emissions where the ZnO nanoparticles act as an oxidation catalyst for the combustion process, converting CO to CO\textsubscript{2}[17,18]; ZnO NP acts as an oxygen buffer at high temperatures inside the combustion cylinder, releasing the necessary oxygen:

\[ \text{ZnO} + \text{CO} \rightarrow \text{Zn} + \text{CO}_2 \] ...

A fluctuation between the curves was observed in this experiment, which may be due to issues with air provision during the tests.

\[ \text{Figure 5. Variation of BTE with Load (bmep) kN/m}^2. \]

4.3.2. Unburnt hydrocarbons.
Figure 6 shows the unburnt hydrocarbon variation vs. engine load. Unburnt hydrocarbon emissions are produced as a result of incomplete combustion, and this emission thus reduces with an increase in load for all fuel blends. NE fuel produced the highest HC emissions at low loads; nevertheless, under increasing loads, HC emissions reduced due to the increase in temperature. The presence of water to create an emulsified fuel causes the fuel to undergo secondary atomisation, which enhances the combustion and reduces HC as compared with net diesel at these higher temperatures.
ZnO NP impact also reduces HC emissions as compared with NE and net diesel fuel. ZnO NP helps to complete the combustion of fuel by lowering the activation temperature of carbon, encouraging complete combustion and the development of high temperatures; it also facilitates access to oxygen due to acting as an oxygen buffer, providing oxygen from its lattice position [19].

![Figure 6. Variation of HC with Load (bmepl kN/m²).](image)

4.3.3. Smoke opacity.
The smoke opacity for all fuel blends varied with the load on the engine, as illustrated in Figure 7, such that increasing the load increased engine smoke opacity for all fuel blends. NE fuel showed reduced smoke opacity as compared to net diesel fuel as a result of secondary atomization from the micro-explosions of NE fuel. Partially burned HC tends to oxidise in the presence of excess oxygen in combustion cylinders, as provided by emulsified fuel. The catalytic effect of nanoparticles enhances the heat transfer rate due to their high surface area/volume ratio and heat conduction properties [22], which increase oxygen availability from the water molecules in the NE fuel. The ZnO NP blended in NE fuel supplied thermal stability and helped to oxidise unburned hydrocarbons and soot particles, reducing the delay in ignition period and allowing faster evaporation. This reduced smoke emissions by minimising the premixed combustion phase and reducing ignition delay [20,21]. Figure 7 shows the reduction in smoke opacity caused by the addition to ZnO NP with increasing dose levels from 50 ppm to 150 ppm due to the small particle size (10 to 30 nm) and high surface area (>60 m²/g) which facilitate the atomisation process.
4.3.4. NOx Emissions.
NOx concentrations for fuel blends with increasing engine loads are shown in Figure 8. This figure illustrates that increasing loads produce more NOx due to increasing the temperature inside the combustion cylinders. The NOx emissions for NE fuel were lower for all loads due to the water content reducing the combustion chamber temperature and preventing formation of NOx, and the different concentrations of ZnO fuel blends showed similar results, with little difference appearing between the curves for various doses of ZnO NP. ZnO reduces the formation of NOx by acting as a catalyst for decomposition, thus forming NO [10].

5. Conclusions
A four-cylinder TD313 direct injection CI engine was used to test five fuels: net diesel, NE fuel, and NE Fuel containing three levels (50, 100 and 150 ppm) of ZnO NP. The combustion emissions and performance characteristics of these ZnO NP blends in NE were thus studied and compared with the results for NE fuel and net diesel. The conclusions of the experimental study can be summarised as follows:

- A reduction in BSFC was observed when using NE containing ZnO NP as compared to pure diesel and NE fuel. NE fuel showed the highest BSFC, at 4.2%, among the fuels tested.
- NE fuel containing 150 ppm ZnO NP showed a 10.2% enhancement in BTE as compared with net diesel fuel and NE fuel.
• Carbon monoxide emissions and unburned hydrocarbons were found to be lower in the presence of ZnO NP in NE as compared with other fuel blends; NE+150ppm ZnO decreased CO and HC emissions by 18% and 17.1%, respectively, due to oxidation effect of the nanoparticles. NE fuel displayed higher CO and HC emissions at low loads, though these were reduced by 4.34% and 4.28%, respectively on increases in the load.

• Significant reductions in NOx and smoke emissions (5.35% and 17.1%, respectively), and a 13.2% further reduction in NOx emissions were found on using 150 ppm ZnO NP dispersed in NE fuel at maximum bmep.

6. Abbreviations

| Symbols | Definitions |
|---------|-------------|
| APS     | Average particle size |
| bmep    | Brake mean effective pressure |
| BP      | Brake power |
| BSFC    | Brake specific fuel consumption |
| BTE     | Break thermal efficiency |
| CI      | Compression ignition |
| CO      | Carbon monoxide |
| CO₂     | Carbon dioxide |
| cSt     | Centistoke |
| DI      | Direct injection |
| HC      | Unburned hydrocarbon |
| HLB     | Hydrophilic lipophilic balance |
| N₂      | Nitrogen |
| NO      | Nitrogen oxide |
| NOx     | Nitrogen oxides |
| PM      | Particulate matter |
| rpm     | Round per minute |
| S80     | Span80 |
| SSA     | Specific surface area |
| T80     | Tween80 |
| NE      | Nanoemulsion |
| ZnO     | Zinc oxide |
| Zn      | Zinc |
| FSN     | Filter smoke number |
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