An experimental investigation of Impact of ZrO$_2$ nanoparticles in DI engine performance

Adel Sharif Hamadi$^1$, Hayder Abed Dhahad$^2$, Ali Ghufran Khidhir$^3$

$^1$Petroleum Technology Department, University of Technology, Baghdad, Iraq.
$^2$Mechanical Engineering Department, University of Technology, Baghdad, Iraq.
$^3$North Gas Company, Ministry of Oil, Kirkuk, Iraq.

1 Adel_al_obaidi@yahoo.com, 2 hayder_abed2002@yahoo.com, 3 ali.ghafran@gmail.com

Abstract

Many investigators have examined the effluent of different types of nanoparticles on emission characteristics and performance of diesel engine but most of the present studies have been concentrated only diesel or biodiesel that contain dispersed nanoparticle. In the present work, water in diesel Nano-emulsified fuel was prepared by high speed rotor-stator homogenizer, and then addition of (50ppm, 100ppm, 150ppm) Zirconium oxide ZrO$_2$ nanoparticle blended water-diesel nanoemulsion (WiDNE). The objective of this project is to evaluate the effect of ZrO$_2$ nanoparticles on combustion characteristics and engine performance. Direct injection (DI), water cooled four cylinders, in-line, natural aspirated Fiat diesel engine was used and run at a constant speed (1500 rpm) and constant fuel injection pressure (400 bars) with varying the operation load. The concentration of the emission gases such as NOx, unburned total hydrocarbon HC, CO and CO$_2$ was measured by Multigas analyzer model 4880. The engine exhaust smoke emissions were measured using the AVL-415 smoke meter. The experimental results notified that WiDNE+ZrO$_2$ fuel imposes the capability to enhance fuel properties, improve the engine efficiency as well as reduction in the emissions concentrations of exhaust gas.

Keywords: diesel fuel, Nanoemulsion, Engine performance, Combustion Emissions.

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دراسة تجريبية لتأثير زركونيوم النانوي ($\text{ZrO}_2$) في أداء محركات الديزل

عادل شريف حمادي$^1$, حيدر عبد ضهيد$^2$, علي غفران خضر$^3$

$^1$قسم تكنولوجية النفط, الجامعة التكنولوجية, بغداد, العراق.
$^2$قسم الهندسة الميكانيكية, الجامعة التكنولوجية, بغداد, العراق.
$^3$شركة غاز الشمال, وزارة النفط, كركوك, العراق.

$^1$Adel_al_obaidi@yahoo.com, $^2$hayder_abed2002@yahoo.com, $^3$ali.ghafran@gmail.com

الملخص

قام العديد من الباحثين بفحص تأثير أنواع مختلفة من الجسيمات النانوية على خصائص الانبعاثات وأداء محرك الديزل ولكن معظم الدراسات الحالية تركزت فقط على الديزل أو وقود الديزل الحيوي الذي يتكون من جسيمات نانوية. في هذا العمل, تم إعداد وقود الديزل مستحمب النانوي بواسطة الخلط عالية السرعة, وبعد ذلك إضافة (05, 100ppm, 150ppm) و Material ZrO$_2$ nanoparticles و مزجه مع وقود المستحضر (WiDNE). الهدف من هذا المشروع هو تقييم تأثير جسيمات ZrO$_2$ على خصائص الاحتراق وأداء المحرك. تم استخدام الحقن المباشر (DI), تبريد مائي من أربعة أسطوانات, ومحرك ديزل فيات, وتشغيله بسرعة ثابتة (1500 دورة في الدقيقة) وضغط حقن الوقود المستمر (400 بار) مع تغيير حقل التشغيل. تم قياس تركيز الغازات المنبعثة مثل أوكسيد النتروجين ومركبات الكربون الهيدروكربونية الكلية و متغوسط Multigas 4880 CO$_2$ و CO و HC غير المحمولة. تم قياس انبعاثات الدخان من المحرك bằng استخدام مقاس الدخان AVL-415-415. واثبتت النتائج التجريبية أن وقود وقود WiDNE + ZrO$_2$ لديه القدرة على تحسين خواص الوقود وتحسين كفاءة المحرك بالإضافة إلى خفض التراكيز غازات العادم.

الكلمات الدالة: وقود الديزل, وقود المستحلب النانوي, كفاءة المحرك, الانبعاثات الاحتراق.

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1. Introduction:

The necessity in air quality enhancements and the existing cost of fuel requires alternative fuels for vehicles and CI engines. The traditional sources of energy are being brought down very quickly and the world is in the direction of a global crisis. The basic task nowadays is exploitation of non-conventional resources of energy for generation of power. Non-conventional fuels are also known as Alternative fuels. Methanol, Biodiesel and Ethanol are alternatives for petroleum and can be used in diesel engines (internal combustion) with very slight or no modification. The day by day, increasing in the use of diesel engine in numerous fields, especially in power generation and agriculture application, increasing the request of diesel fuel, due to lack of green spaces in Iraq and the large number of factories, toxic emissions of transport and high temperatures in a long summer lead to global warming, made challenge to reduce these emissions. Severe rules on emission of diesel engine are promoting to the use of alternate fuels and emissions reduction technique. Environmental Air quality and human health concerns have driven the legislation to other emissions of internal combustion engine, with significant consideration paid to particulate matter and nitrogen oxides (NOx, PM) [1]. Short-term exposing to high concentrations of NO2 can cause inflammation of the air ways and more longer term exposure to low levels, increasing capability to respiratory toxicities and to allergens, and nitrogen oxides are known precursors to photochemical smog .Further rigid regulations on exhaust gas emissions drives a foremost research endeavor in engine improvement in order to diminish these pollutants [2].

The most control strategy of the NOx depends on lowering the heat of combustion or decreasing the duration time of the diffusion flame period, due to the thermal dependent of the NO formation and therefore NOx compounds [3]. Water in diesel Emulsions for use in engines (internal combustion) are simply applicable alternate fuels for the present vehicles. The emulsified fuel is defined as dispersion of water in conventional diesel with a certain surfactants, additives, for stabilizing water droplets in the system. There is a great interesting in the use of water in diesel emulsions and the main reason is due to the importance of the environment. Existence of water droplets has an important impact on several emission components: exhaust gases such as nitrogen oxides (both NO and NO2, which are collectively referred to as NOx) and carbon monoxide (CO), as well as particulate matter and black smoke [4]. The water and Diesel fuel with water content normally range from 10% to 20%. 
Their generally consistent conclusion is that the right water ratio of emulsified diesel can improve the fuel economy and emissions of diesel engine [5, 6]. Addition of Nano fluids along with the emulsified fuel and using it as fuel finds attraction for improving the performance of the diesel engine further. In the present work, influence of a Nano fluid on the emission and performance parameters of a compression ignition engine fuelled with water diesel Nano fluid emulsion was studied experimentally. An exciting concept for improving combustion of the traditional liquid fuels is the use of energetic materials in Nano scale as additives for fuel.

2. Materials and Methods:

2.1 Used Surfactants:

Span 80 with HLB (hydrophilic lipophilic balance) 4.3 and Tween 80 with HLB 15 are two surfactants that are used in the present work Fig. 1. Specifications of the both the surfactants are shown in Table 1. The formula used to calculate the HLB value is given as:

\[
\text{HLB} = \frac{\text{Hydrophilic A.} \times \text{Hydrophilic B.}}{\text{Hydrophobic A.} \times \text{Hydrophobic B.}}
\]
2.2 Diesel Fuel Properties:

Conventional diesel fuel (South Petroleum Company, Basra, Iraq) was used (from Dura Refinery, Baghdad, Iraq) as the continuous phase of emulsion. The physical properties of used diesel fuel are shown in Table 2.

Table 2: Physicochemical properties of diesel fuel.

| NO. | Properties                                      | Value   |
|-----|------------------------------------------------|---------|
| 1   | Density at 15°C (Kg/m³)                         | 0.8932  |
| 2   | Total sulphur (%wt)                             | 2.88    |
| 3   | Total Nitrogen(ppm wt)                          | 320     |
| 4   | Acidity (mg KOH/g)                              | 0.1     |
| 5   | Aniline point (°C)                              | 71.8    |

2.3 Experiment Details:

The pure diesel, WiDNE fuel with and WiDNE+ZrO₂ at different nanoparticle level were charged into a variable CI diesel engine at compression ratio 17 for analyzing its behavior. The engine was coupled to a hydraulic dynamometer through which the load was applied by increasing the torque. Multigas model 4880 emissions analyzer was used to measure the concentration of NOx, unburned HC, CO₂ and CO. The engine exhaust smoke emissions were measured using the AVL – 415 smoke meters. Table 3 shows the specifications of the exhaust gas analyzer.

Table 3: Specification of the exhaust gas analyzer.

| Measurement principle | Measurement of filter paper blackening |
|-----------------------|----------------------------------------|
| Measurement range     | 0 to 10 FSN                            |
| Detection limit       | 0.002 FSN or ~ 0.02 mg/m³              |
| Resolution            | 0.001 FSN or 0.01 mg/m³               |
| Repeatability         | 10sec intake time                      |
2.4 Fuel Preparation:

In this study, technical-grade diesel fuel was provided by Dura-Refinery and used as the continuous phase in nanoemulsion fuel. Mixed surfactant (lipophilic Surfactant) of S80 with HLB= 4.3 and T80 (hydrophilic surfactant) to reach minimum interfacial tension and for stabilizing water dispersed in courthouse phase. The concentration of mixed surfactant is 5% wt% with HLB equal to 6, mixed to diesel fuel and mixing by using rotator-stator for 5 min and at 5000 rpm homogenizing speed, after then water 12% wt% with pH=10.8 are added to a blend of diesel and mixed surfactant and mixed for 30 min further. Droplet diameters are measured by DLS (dynamic light scattering) technique using particle size analyzer a Brookhaven 90Plus instrument. Addition of water will change from properties of diesel fuel as shown in Fig. 2.

![Droplet Diameter of Prepared Nanoemulsion](image)

**Fig. 2:** Droplet diameter of prepared nanoemulsion.

Calorific value (kJ/kg) value of both WiDNE and pure diesel are measured by Bomb calorimeter (PARR 1266), it is found that replacement of 12 wt% water by net diesel contributed of reducing calorific value from 44800(kj/kg) to 38850 (kj/kg) .Water content are reducing heat of reaction and so help to reduce the emissions especially NOx. The Viscosity of diesel is increased by water present in WiDNE from 3.286 cSt to 4.56 cSt at 40°C. Higher viscosity may lead to too viscous and make it not pumped or ignite. Flash point is an indicate for fuel volatility, it increased from 54 °C for diesel to 61 °C with respect to 12 wt% of water. It is known that water is heavier than the diesel fuel, water in diesel fuel associated to increase density from 0.87 g/cm³ to 0.882 g/cm³. Water content in emulsified diesel fuel caused reduction in pour point from 9°C to 7°C .With formation of WiDNE fuel; this pour point can be lowered significantly in order to confirm safe transportation of these types of oils. ZrO₂ nanoparticle dispersed into WiDNE fuel at 50 ppm, 100 ppm and 150ppm nanoparticle concentration for another 15 minutes
to assure complete distribution into the nanoemulsion in Fig. 3 shows combustion mechanism of additives with the WiDNE.

![Combustion Mechanism Diagram](image)

**Fig. 3:** Schematic illustration of combustion mechanism of Nano-additive in emulsion inside the fuel chamber of the diesel engine. [14].

ZrO$_2$ nanoparticle used to study the effect of nanoparticle dispersed into WiDNE on CI engine. Table 4 shows the specifications of ZrO$_2$ nanoparticle. (Supplied by sky spring company, USA).

**Table 4:** Specification of ZrO$_2$ nanoparticle.

| Item            | Specification                  |
|-----------------|--------------------------------|
| Purity          | 99.9%                          |
| Appearance      | white nanopowder               |
| APS             | 20~30nm                        |
| Boiling Point   | 4300 °C                        |
| Melting Point   | 2715°C                         |
| SSA (m$^2$/g)   | > 40                           |
3. Results and Discussion:

3.1 Performance Characteristics:

3.1.1 Brake Power (BP):

The experiments on the BSFC on diesel engine were carried with net diesel fuel and four mixture of (WiDNE, WiDNE + ZrO$_2$.50 ppm, WiDNE + ZrO$_2$.100 ppm and WiDNE + ZrO$_2$.150 ppm) with compression ratio 17. During the experimentation, the load on the engine was varied from 5 to 15 kg with 2.5 kg step size at constant speed 1500 rpm. Four cylinders, two valve, in-line, natural aspirated Fiat diesel engine was used in this work to test the fuel and its detailed specification is listed down in Table 5. The photograph of diesel engine is shown in Fig.4.

Table 5: CI Engine Specification.

| Engine type | 4cyl., 4-stroke |
|-------------|----------------|
| Engine model | TD 313 Diesel engine reg |
| Combustion type | DI, water cooled, natural aspirated |
| Displacement volume | 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 dia. (0.48mm) , Spray angle= 1600, Nozzle opening pressure=40MPa |
It was perceived that the BSFC decreased when the load was increased for all processes of diesel and Nanoemulsions blends, as shown in Fig. 3 due to the consumption of more fuel [7]. It is observed that WiDNE shows higher BSFC as compared to conventional diesel and nanoparticle blended water in diesel Nanoemulsions. This is maybe due to the higher viscosity and lower heating value of water diesel emulsions as compared with diesel [8, 9].

It was also observed that BSFC decreases when nanoparticle volume fraction in the Nanoemulsions blend was increased for any given load. This reduction in fuel consumption can be due to increase in calorific value with the addition of the nanoparticle [10, 11]. Potential advantage of the water in diesel Nanoemulsions fuels is the integrated influence of secondary atomization and micro-explosion phenomenon, resulting in strong vaporization and mixing better of air, turns in improving the combustion reactions inside the engine cylinders. Influence of ZrO$_2$ on BSFC was investigated and it is illustrated through Fig.5. There was an apparent effect on reduction of BSFC with increasing of ZrO$_2$ concentration in WiDNE. Due to high catalytic activity of ZrO$_2$ nanoparticles blended fuels, which facilitate improved combustion and improved combustion characteristics[15]. With increasing of ZrO$_2$ from 50 ppm to 150 ppm, BSFC reduced. The effect of 50 ppm of ZrO$_2$ blended in WiDNE is barely recognized when compared with the net diesel but it is more effective for BSFC reduction with increasing concentration.
3.1.2 Brake Thermal Efficiency (BTE):

It was perceived that (BTE) increased when the load was increased for all operations of diesel and nanoemulsion blends as obvious in below Fig.6. It was observed that the conventional diesel shows lower Brake thermal efficiency as compared to WiDNE and nanoparticle blended water in diesel Nanoemulsions [8, 9].

**Fig. 5**: Alteration of BSFC with respect to Load (bmepr) kN/m² with addition of ZrO₂ nanoparticles.

**Fig. 6**: Alteration of BTE with respect to Load (bmepr) kN/m² with addition of ZrO₂ nanoparticles.
From Fig. 6 it is obvious that the increase of thermal efficiency of WiDNE on net diesel fuel. The enhancement of thermal efficiency was observed with ZrO$_2$ nanoparticles. There was an apparent effect on increasing of thermal efficiency with increasing of ZrO$_2$ concentration in WiDNE. With increasing of ZrO$_2$ from 50 ppm to 150 ppm, the thermal efficiency increased.

### 3.2 Exhaust Emission Analysis:

#### 3.2.1 Nitrogen Oxide (NOx):

The experiments on the NOx emission by diesel engine were carried with net diesel fuel and four mixtures of water in diesel nanoemulsion (WiDNE, WiDNE + ZrO$_2$.50 ppm, WiDNE + ZrO$_2$.100 ppm and WiDNE + ZrO$_2$.150 ppm) with compression ratio 17. During the experiments, the load on the diesel engine was changed from 5 to 15 kg with 2.5 kg step size at constant speed 1500 rpm. It was noticed that the NOx emission increases when the load was increasing with the all operations of diesel and Nanoemulsion blends as shown in below Fig.7. It is observed that WiDNE reduces NOx emission as compared to conventional diesel. Water molecules presents in emulsified fuel possess very high latent heat of vaporization, which tends to reduce the peak cycle temperature, hence oxides of nitrogen emission of water diesel nanoemulsion were found on the lower side as compared to diesel fuel for all the power output.

It is discovered that the water in diesel emulsion with 15% water content produces the less amount of NOx emission as compared to the net diesel fuels [12]. It was also observed that the NOx emission gives effects when the nanoparticle volume fraction in the nanoemulsion blend was increased. It is observed that the nanoparticles addition to diesel fuel decreases the NOx emission [13]. Influence of ZrO$_2$ on NOx emission was studied and it is shown through Fig. 5. There was a little reduction in NOx emission with increasing of ZrO$_2$ concentration in WiDNE. With increasing of ZrO$_2$ from 50 ppm to 150 ppm, the NOx emission decreased.
Fig. 7: Alteration of NOx emission with respect to Load (bmeP) kN/m² with addition of ZrO₂ nanoparticles.

3.2.2 Smoke Opacity:

Diesel fuel showed the higher magnitude of Smoke opacity over the entire load range. It was noticed that the Smoke opacity increased when the load was increased for all operations of diesel and Nanoemulsion mixers, as shown in below Fig. 8.

Fig. 8: Alteration of Smoke opacity with respect to Load (bmeP) kN/m² with addition of ZrO₂ nanoparticles.
It is observed that WiDNE reduces Smoke opacity as compared to conventional diesel. Micro explosions of emulsified fuel result in secondary atomization of injected fuel which ends up with reduced smoke intensity as compared to diesel fuel as illustrated in Fig.3. The presence of nanoparticle in the emulsion tends to separate the oxygen atom in the water molecule which rises up the availability of oxygen. Excess oxygen present in the combustion chamber tends to oxidize the partially burned hydrocarbon; thereby reduced smoke intensity is witnessed for water diesel nanoemulsion as compared to diesel for all power outputs. It was also observed that Smoke opacity reduced when nanoparticle volume fraction in the nanoemulsion blend was increased.

Effect of ZrO$_2$ blending with nanoemulsion caused a decrease in the Smoke opacity compared with pure diesel and WiDNE. It is obvious from Fig.8.that Smoke opacity decreased when blending ZrO$_2$ in nanoemulsion with increasing its concentration from 50 ppm to 150 ppm.

3.2.3 Carbon Monoxide (CO):

Carbon dioxides are coming as exhaust resulting from combustion of CO inside cylinder and complete combustion of carbon particles of the fuel. Carbon monoxide is extremely depending upon the air-to-fuel ratio comparing with stoichiometric ratio. In most cases, CI engine functions with lean mixture and thus results in lower CO emission. It was noticed that the CO emission decreased when the load was increased for all operations of diesel and Nanoemulsion blends, as shown in below Fig.9.

WiDNE fuel showed the higher magnitude of CO emission over the entire load range. It was also observed that the CO emission decreased when nanoparticle volume fraction in the Nanoemulsions blend was decreased for any given load. This reduction in CO emission because of nanoparticles will easily separate the oxygen atom from the water molecule which ensures complete oxidation of fuel droplets. In addition to it better air and fuel mixing rate was achieved inside the combustion chamber due to finer atomization of emulsified fuel droplets, which ends up with complete combustion.
Fig. 9: Alteration of CO with respect to Load (bme) kN/m² with addition of ZrO₂ nanoparticles.

Decreasing in CO emission was observed from Fig.9 when blending ZrO₂ nanoparticles with WiDNE. Surface area of ZrO₂ is 20-30 nm which makes it easier for atomization process.

3.2.4 Unburned Hydrocarbon (HC):

HC emissions are producing due to the incompletion combustion and they tend to decline with load increasing. The total HC emissions are commonly made as a consequence of flame quenching. The formation of higher HC and CO emissions is extremely relied on the viscosity of fuel. More viscosity is also leading to longer spray penetration rate. The formation of higher HC emissions is due to the wetting cylinder of engine by incomplete combustion. It was observed that the HC emission decreased when the load was increased for diesel and Nanoemulsions blends as shown in Fig.10 due to the increase of combustion temperature. It is observed that WiDNE showed higher HC emission as compared to conventional diesel and nanoparticle blended water in diesel Nanoemulsions.

It was also noticed that the HC emission decreased as nanoparticle volume fraction in the Nanoemulsions blend was increased for all loads. At peak load condition, the HC emission of water diesel Nanoemulsions was quite higher than diesel fuel.
Fig. 10: Alteration of Unburned Hydrocarbon with respect to Load (bmep) kN/m² with addition of ZrO₂ nanoparticles.

These Fig.10 show that at low load situation, the HC emission of diesel was less than WiDNE. With increasing the load, the HC emission will reduce with increasing the load. At high load the emissions by WiDNE will be less.

When using diesel fuel, there is a small increase of HC emission with increasing the load, but the curve will back down to become less than the net diesel in HC emission. The improvement of HC emission was observed with ZrO₂ nanoparticle blended with nanoemulsion in their respective concentration, as in Fig. 8.

3.2. 5 Viscosity:

The higher temperature, the greater kinetic energy is for the emulsion particles. This continued increase increases the collisions of the molecules with each other and thus leads to a decrease in fluid viscosity, as clarified in Fig.11.
It was observed that viscosity of emulsion fuel decreases when the temperature increasing. The effect of lower viscosity decreases as the temperature rises and upon arrival to the stage, there is no heat effect for the viscosity.

All experiments were done in 60 seconds and 100 rpm for spindle rotating inside the fluid. Above 100°C, water begins to boil and separate from the nanoemulsion.

4. Conclusions:

Major purpose of this study is the comparative analysis of WiDNE and WiDNE+ZrO₂ nanoparticle on emission characteristics and engine performance of 4 strokes, CI diesel engine.

4.1 Performance Characteristics:

1. An inefficient increase in BP is detected with the addition of ZrO₂ nanoparticles. Modicum decrease BSFC could be noticed between WiDNE+ZrO₂ .100ppm and WiDNE +ZrO₂ .150ppm.

2. Comprising to other fuels, WiDNE +ZrO₂ .150ppm shows higher BTE. But at higher loads it is look the same effect of WiDNE +ZrO₂ .150.

3. Enhancement in BSFC is obtained with the addition of ZrO₂ nanoparticles.

Fig. 11: Effect of temperature on the viscosity.
4.2 Emission Characteristics:

1. Decrease in NOx emission is noticed with the dispersion of ZrO$_2$ nanoparticle into diesel fuel as comparison to pure diesel or WiDNE fuel.

2. WiDNE contributed large extent to reduce the NOx emissions.

3. ZrO$_2$ nanoparticles reduces the smoke opacity, but is in very limited range when increasing its concentration in WiDNE fuel.

4. More CO emission are obtained in WiDNE fuel, addition of ZrO$_2$ nanoparticles enhanced from CO emissions, but faces some fluctuations with increasing load of engine.

5. ZrO$_2$ nanoparticles have very narrow or don’t have any effect on reducing HC emissions.

6. Viscosity of WiDNE fuel decreases with rising of the temperature to a specific limit.

5. Recommendation:

1. The long stability term of mixtures with different types of emulsifiers was not searched, and there is aim for study of long stability term of different emulsifier blends.

2. The durability and performance of engine were tested for a small period of time, so there is a scope to investigate the durability of the engine on these blends with prolonged operation.

3. Filtration of emission for reusing the nanoparticles and preventing them from releasing in environment.

4. Use of renewable surfactants in emulsion fuels.

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