



Investigation of Impact of CeO₂ nanoparticles blended in Nano-emulsion on efficiency and exhaust emission of diesel engine

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Abstract

Cerium oxide (CeO₂) nanoparticle was added to prepared water in diesel Nano-emulsion to study its effect on exhaust emission and performance of diesel engine characteristics between neat diesel, Nano-emulsion and Nano-emulsion+ CeO₂. Since water and diesel are immiscible, mixed span and Tween 80 surfactants are used for preparation of stable Nano-emulsion. Central composite design, Response surface method is used for optimization process of preparation of Nano-emulsion at optimum suitable condition designed by Design Expert software.

Dispersed Water present of Nano size effect directly on diesel fuel characteristics in compression ignition engine, contributes on reduction of NO_x and smoke emission and better thermal efficiency, but accompanied by little increase in HC and CO emission and fuel consumption.

CeO₂ nanoparticles at three levels (50, 100 and 150 ppm) to optimize Nano-emulsion added and mixed by high energy homogenizer. All diesel, Nano-emulsion and Nano-emulsion+ CeO₂ are examined by Engine run at 400 bar and 1500 rpm with different load.

Improvement in reduction fuel consumption and thermal efficiency are obtained. Exhaust emission (NO_x, HC and CO) and smoke reduced much more are observed with CeO₂ nanoparticle.

Keywords: CeO₂ Nanoparticles, Internal Combustion Engine, Nano-Emulsion

1. Introduction

Diesel engine plays a considerable role in different fields of industries and technologies in internationally. It could be in production machine or in transportation etc., with increasing in applications of diesel resources impact on environment which is leading to greenhouse effects. Emission exhaust gases of diesel engine consider one of the main sources of air pollution, especially in crowded and industrial areas, and it has been a main concern of public for a long time. [1] Solutions are found for environment pollution reduction by emissions of diesel engine that makes it critical concern of investigators [11].

Emulsification technique regards one of the effective methods using for reduction emission of exhaust gases from diesel engine motivated by its cheap cost [2]. The suspended water droplets of emulsified fuel by suitable surfactant don't allow direct contact of water with the inside surfaces of engine [3]. Water in diesel emulsion formulation is confirmed to minimum (NO_x, HC, SO_x, CO) emissions and (PM) particulate matter without recompensing performance of diesel engines [4].

Water vaporization of diesel emulsion fuel helps to decreasing the local flame adiabatic temperature which is the chemical reaction temperature for formation of NO in gas phase. [5, 6].

Volatility difference between water and diesel and the water boiling point is lower than the oil, during compression in piston while the temperature is increasing, droplets of water in emulsion exhibit explosive evaporation and diffusing of surrounding oil layers [7].

Huge number of tiny secondary droplets are produced due to secondary atomization induced by these explosions. Secondary explosion is also known "Micro explosion" [8]. Improvement in combustion efficiency and reduction in pollutant exhaust emissions is due to the Micro explosion that enhance the mixing of inlet air and fuel during combustion [7].

When the droplet size of dispersed phase is between 20-500 nm it is known as Nano emulsion. Both high (high-shear stirring, high-pressure homogenizers, or ultrasound generators) [13] and low (phase inversion temperature (PIT)) [9, 14, 15] energy methods are used to produce kinetically stable emulsion.

Better stability can obtain in Nano emulsion droplet aggregation and gravitational separation due to its smaller droplet size in comparison with Micro and macro emulsion [10].

Water in diesel Nano emulsion preparation including three basic composition: continuous phase diesel, dispersed phase water and mixture of emulsifiers. Selection of suitable surfactant contribute have great impact to produce Nano emulsion fuel keeping fine droplet of water in diesel for much longer time. Hydrophilic-lipophilic balance of the produced emulsion should be chosen 4-6 and according to specific equation [16].

More water fine droplets and more surface area of Nano emulsion in comparison with microemulsion due to its smaller droplets size [12], participating more effectively in fuel/air mixing for complete combustion.

Brake specific fuel consumption of emulsion fuel is higher than net diesel because of the lower heating value of emulsion fuel due to presence of quantity of water [17, 18].

For obtaining emulsion with higher stability and less exhaust emission as a fuel, its component percentage should be at optimum content. Performance and starting ignition problems of fuel take place if too much water percent present in emulsion fuel [19]. Addition of water to certain limit had positive effect, but continuing in increasing water percent decrease emulsion stability [20]. The reason behind of the increasing emission of larger amount of CO concentration and engine efficiency problems is too much loss in latent heat in combustion of fuel to completely burn [21, 22].

Nano emulsion has taken attention a lot of investigators of use as fuel emulsion as a potential source of energy in compression combustion engine due to its supplying minimum emission and contribute to convert CO to CO₂ than the regular fuels [1, 17, 18, 23]. Several of investigations proved that addition nanofluids can enhance the combustion efficiency and reduce emissions. [24, 25, 26].

Nano Metal oxides such as copper, cerium and iron are regarded fuel additives. Metal nanofluids can react with water molecule for enhance the oxidation of soot or can react directly with carbon atoms in soot for minimizing the oxidation temperature [27]. Providing more oxygen for combustion process due to Ability of CeO₂ nanoparticles act like oxygen buffers source, oxidation of hydrocarbons in fuel concurrently, therefore lowering the nitrogen oxides, especially at stoichiometric condition [25].

High oxygen storage capacity and mobility inside its lattice and ease changing between Ce³⁺ and Ce⁴⁺ states. All these properties and multitude cerium in earth, high effectively and low cost makes it better alternative to other metal oxides nanoparticles [28,29]. The major aim of

this study is finding out optimum condition of preparing Nano-emulsion and the impact of CeO₂ nanoparticle on the efficiency and exhaust gases emissions of diesel engine.

2. Materials

Preparation of Nano-emulsions in experiments were done by distilled water at 25°C. lipophilic surfactant of span 80 are mixed with higher molecular weight hydrophilic emulsifier Tween 80 to increase HLB value. Continues phase of diesel are provided by Dora Refinery in Baghdad for Nano emulsified fuel. Table (1) shows the properties of diesel fuel.

Table (1) Properties of diesel fuel.

NO.	Properties	Value
1	Density at 15 °C (Kg/m ³)	0.87
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

2.1 Preparation and characterization of Nano emulsion

Six parameters chosen to study their effects on the prepared Nano emulsion and interaction between the variables to the stability of optimized sample. Response surface method with 54 runs are built by Design Expert software version 10 for preparation of different Nano emulsions with varying the variables in each run. Water content is varying between (0-25 wt%) with pH range from (7-14) at basic circumference. After preparation of mixed surfactants, the accepted value of hydrophilic-lipophilic balance for water in oil emulsion is chosen to be (4.5-6.5) at (1-5 wt%) content of emulsifiers. High energy method is established by high speed rotator-stator Heidolph DIAX 900 homogenizer for rupture water phase to nanometer size. Figure (1) shows optimum preparation circumstances of nano emulsion.

CeO₂ are added to net diesel and put on rotating speed 1500 round per minute for 30 minutes. Surfactants are mixed for certain HLB 6 preparation and mixed with the diesel that carrying CeO₂ nanoparticles, this step takes 10 minutes with 5000 rpm. last step is based according to instruction of optimum condition: water percent is 12 wt% of the system with pH equal to 10.5.

Blending speed is 15000 rpm for 30 minutes. All experiments of the process are carried out at 25°C.

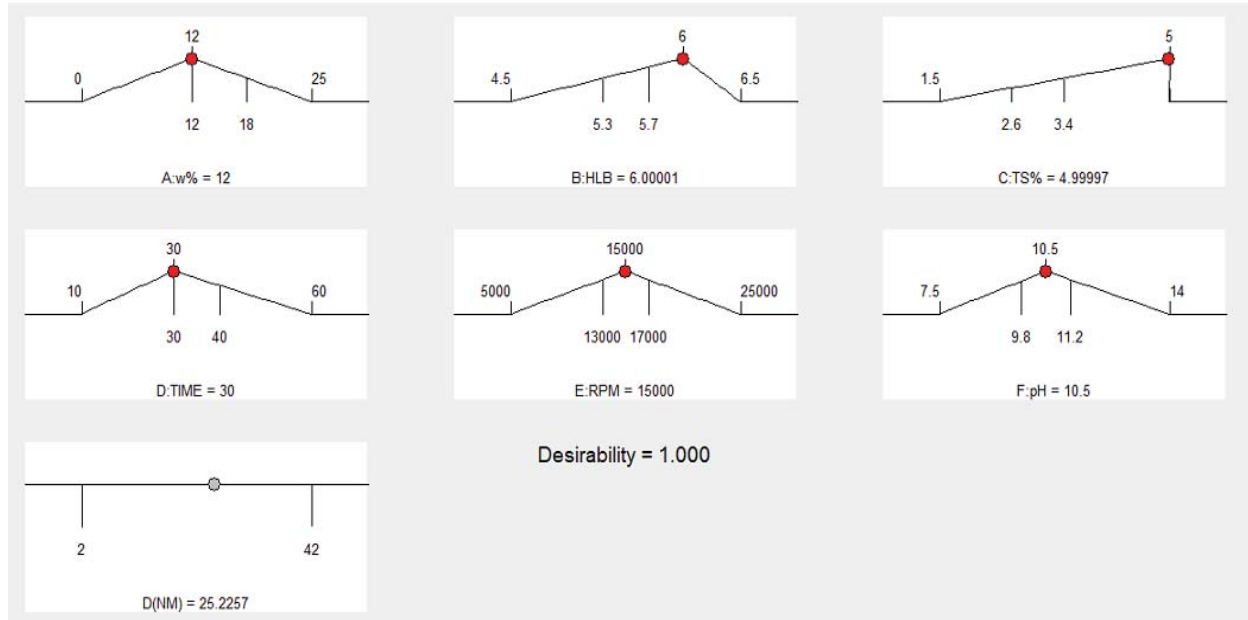


Fig. (1) Optimum condition preparation of Nano-emulsion.

2.2 Droplet size distribution Analysis:

Hydrodynamic diameter and size distribution for water droplets by the technique of dynamic light scattering using (Brookhaven 90 Plus) instrument. Each test of sample takes 3 minutes at 25°C.

2.3 Viscosity measurement

For measuring viscosity of emulsified fuel Brookfield viscometer was used. The RV7 spindle is used. The capacity of the sample is 100 ml and temperatures are varying from 25°C to 100 °C to study the effect of the temperature on emulsifier's fuel viscosity.

2.4 Calorific Value Measurement

PARR 1266 instrument, isopribol bomb calorimeter was used to determine the gross heat combustion of an emulsified diesel fuel test. The heat obtained fromk emulsified fuel is compared with the heat obtained from the combustion in same quantity of Benzoic acid sample that its calorific value is known.

The gross calorific value of emulsified fuel is in equation (1):

$$HC = (WT - e1 - e2 - e3)/ M \dots\dots\dots (1)$$

W: energy coefficient of the device

T: rise in temperature

e 1: the amount of heat producing by the conversion of the nitrogen in the oxygen to the nitric acid

e 2: produced heat by sulfuric acid if the form contains sulfuric acid

e 3: resulting heat of fusion of the blast wire

M: mass of sample in grams

2.5 Flash point Determination

For determination Flash point of an emulsified fuel Pensky Martin (Closed Cup) Apparatus is used. Fire point is known the temperature at which the sample of oil starts to fire continuously for minimum 5 seconds.

3. Combustion Analysis of Prepared W/D Nano emulsion

Diesel engine model (TD 313 Diesel engine rig) four-cylinder, water cooled, natural aspirated with bore and stroke size 100,110 mm at 17 compression ratio and is used for determination and computation of BSFC, thermal efficiency and exhaust gas emission from combustion of the prepared fuels. The tests are carried out at constant speed 1500 rpm, which is the load on the diesel engine, was varying from 5 to 15 kg with 2.5 kg step size.

The concentration of five gases: unburned hydrocarbons, CO, CO₂, O₂ and NO_x are measured by automotive emissions analyzer model HG-550 provided by EGMA company.

For measuring the oxygen and nitrogen oxides Electro chemical technique used and for the rest of gases NDIR (Non-dispersive infrared) is the measuring method.

Smoke emissions from the combustion of the fuels are measured by (AVL-415) smoke meter. Filter smoke number (FSN) is the measure unit of Smoke meter which is based on thermodesorption and particle counting on filtrated paper.

3. Results and Discussion

3.1 Characterization of Nano emulsion

The difference in calorific value between pure diesel and emulsified fuel 12% water content is shown in Table (2). Replacement in Nano emulsion fuel by water instead of diesel participates to reduce formation of NO_x by minimizing of reaction temperature, thus exhaust emission and soot formation is also reduced. The improvement in calorific value of emulsions could be

observed with the addition of nanoparticles [30, 31]. It is known higher molecular weight of petroleum fractions have higher flash point and flash point is an indicator for fuel volatility. Water present in Nano emulsified fuel increasing its flash point, depicted in Table (1), Nano emulsion molecule had a higher molecular weight comparing with net diesel. Viscosity of the prepared Nano emulsion had higher value than net diesel. High viscosity results in poor atomization in engine cylinders and combustion of fuel. Density of net diesel are less than the prepared Nano emulsion while pour point is changed from +9 to +7. Problems could take place of high pour point fuels during transporting in pipes. Table (2) illustrated the change in fuel properties as a result of water addition and Nano emulsion formation.

Table (2) Comparison between Nano emulsion and diesel fuel.

Properties (measured)	Diesel fuel	Nanoemilsion fuel
Calorific value (kj/kg)	44800	38850
Flash point (°C)	54	61
Viscosity at 40 °C (cSt)	3.268	4.56
Pour point (°C)	9+	7+
Density (g/cm ³)	0.87	0.882

3.2 Exhaust Emission Gas Concentration

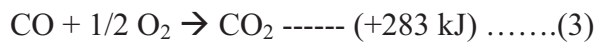
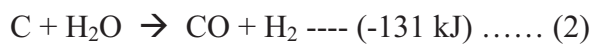
After optimization process and analyzation of factors the present result gained: increasing water content effect on increasing of droplet size, while mixing speed are contribute to certain limit in minimizing of water droplet dispersion size. Emulsifier with 6 HLB saved highly stability of the system at 5 wt% content. Water for the Nano emulsion at base side with pH 10.5.

Figures (2) (a,b,c,d) shows the emissions variation with increasing load on diesel engine (break mean effective pressure) of net diesel and Nano emulsion diesel fuel and blends of Nano emulsion fuel with the level of CeO₂ (50,100.150) ppm at compression ratio 17. All tests are done at constant speed 1500 rpm from 5 Kg to 15 Kg load with 2.5 increasing regularly in each step.

Figure (2a) shows the concentrations of CO emissions of different diesel fuel blends. With increase in load on engine, general decrease in 19.7% CO at 352.88 kN/m² emissions are noticed. At the beginning point of starting fuel ignition due to presence of water content in

Nano emulsion fuel, higher carbon monoxide emission exhausted. High heat sink in the temperature of exhaust are obtained water phase in emulsion.

Atomizing of diesel fuel by the secondary explosion a rounded the water nanosized droplets due to phenomenon of Micro explosion result in less burning time, heat sink and enhance of diesel fuel / air blending which obtain complete combustion at less temperature. Oxygen requirement from the outside are reduced due to reaction of the carbon with the oxygen in water. Equations 2 and 3 are describing reactions between water and gas of diesel emulsified fuel.



Equation 3 describing (WGSR) Water gas shift reaction, which using ceria as a catalyst for this reaction for water vapor and carbon monoxide for carbon dioxide formation.

By increasing the load on the diesel engine, CO emission by Nano emulsion is minimized, controversy with the starting point. In Figure (2a), shows the curve of WiDNE are reducing the carbon monoxide more efficiently than the net diesel.

Hydrocarbon emission is the result of the incomplete combustion of the fuel. Increasing the load reducing the HC emission.net diesel at low load are burn better than the emulsified diesel but at higher loads water phase contribute effectively in complete burning and the reducing HC emission 18.5% at higher load.CO and HC emission are producing from the same reason and highly depending on the viscosity of the fuel. Water in diesel Nano emulsion containing 150 ppm CeO₂ is less emission of HC and CO comparing to another fuel blends as shown in Figure (2b). [32, 33].

The source of the emission of the nitrogen oxide is form the outside 78% from the environment air mixture. When the temperature inside the cylinder is increased, monoatomic N are produced from the rupture of the N₂. At high temperature 2500 to 3000 K considerable amount of the monoxide nitrogen are produced, which more NO_x produced. Water content in the WiDNE are showed less NO_x emission and this rate of reducing increase by presence of CeO₂ nanoparticles. Depicted as in figure 3c reduction of NO_x emission from 1381 to 1123 by increasing the amount of CeO₂ nanoparticles from 50 to 150 pp. This result corresponds which proved high reduction in NO_x emission 61% with the surfactant concentration 0.4% and water 0.1% [32].

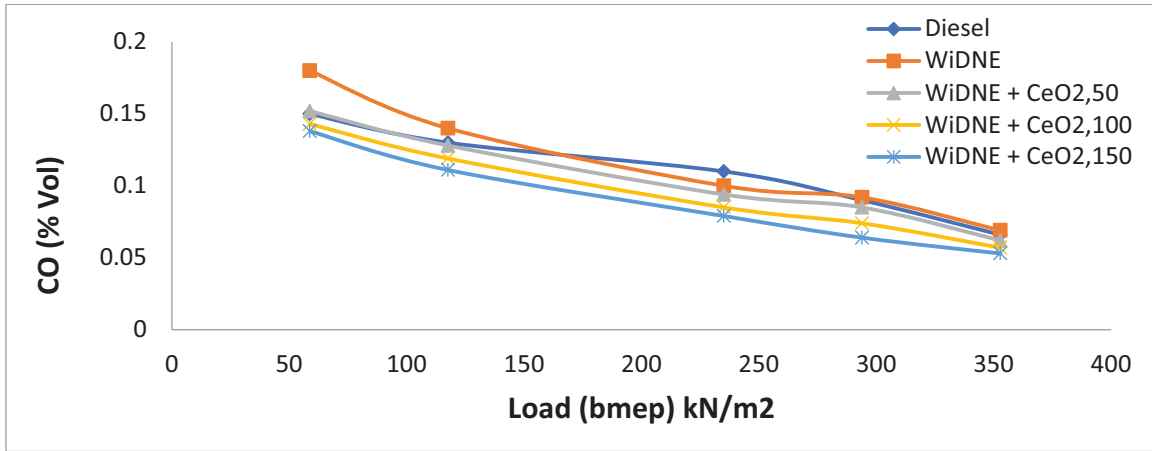


Fig. (2a) Variation of CO to Load (bmep) kN/m²

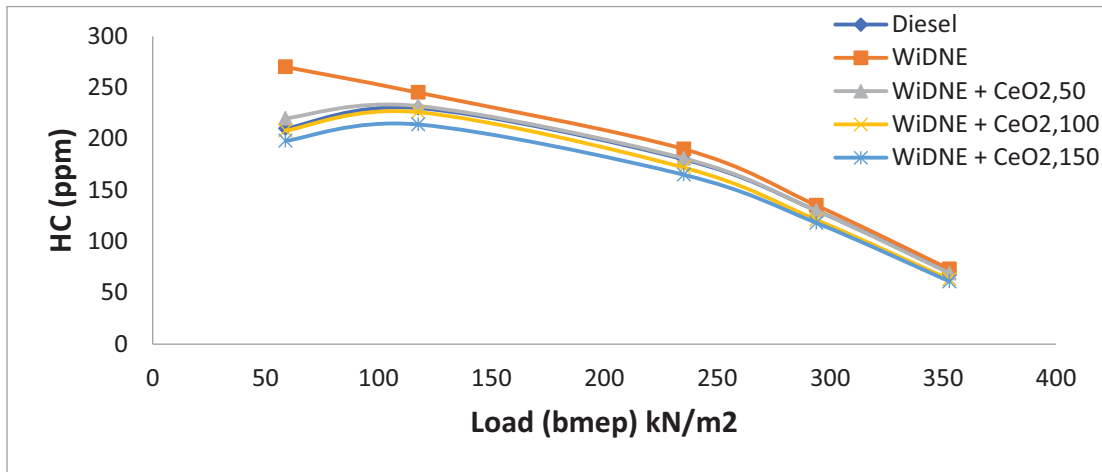


Fig. (2b) Variation of HC to Load (bmep) kN/m²

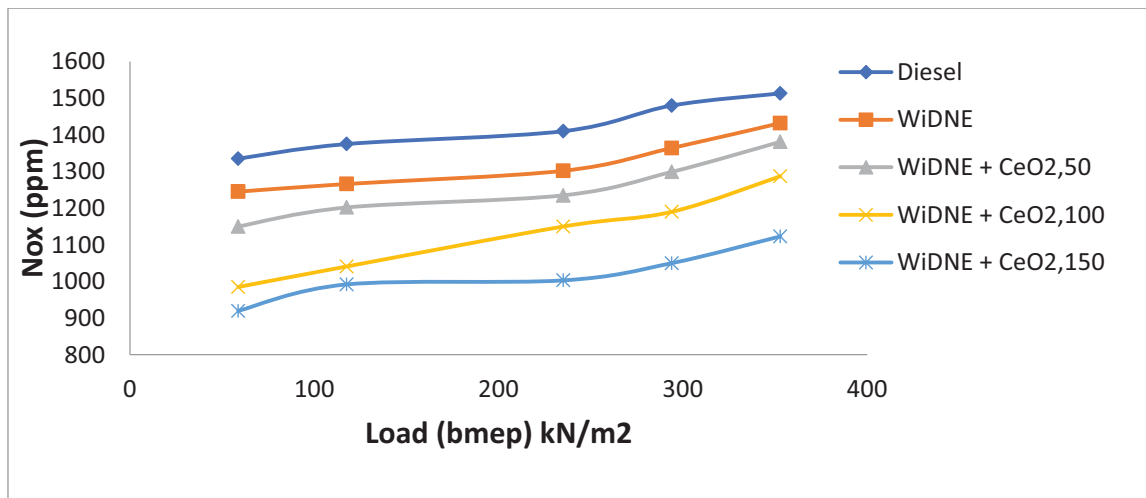


Fig. (2c) Variation of NOx to Load (bmep) kN/m²

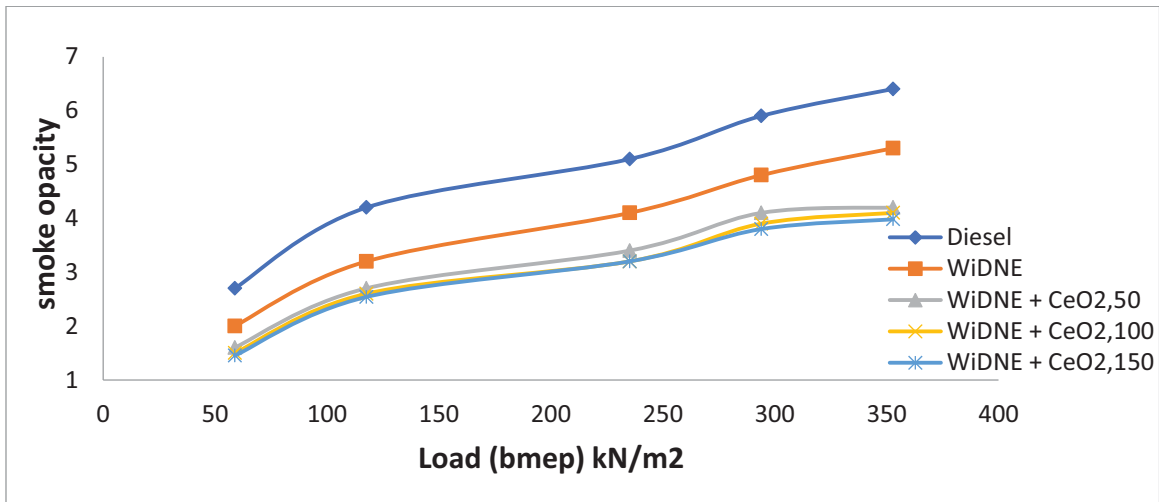


Fig. (2d) Variation of Smoke to Load (bmep) kN/m²

High thermal stability of Ce_2O_3 which let it formed from the oxidation of the hydrocarbons. When there is a lack of oxygen in engine cylinder, CeO_2 are reduced to Ce_2O_3 to provide necessary oxygen for converting carbon monoxide to carbon dioxide [33]. It will re-oxidized to CeO_2 soon as soon when there is enough available oxygen in exhaust gases. This oxygen is provided by the reduction of the NO this time according to the equation 4:



Thus, the amount of the emission of the Nitrogen oxides are reduced by the nanoparticles. Figure (3d) shows the variation of the smoke opacity with the load on the engine, higher Smoke produced by increasing the load. Effect of Nano emulsion was obvious in minimizing 40.6% of the smoke opacity by the effect of Nano emulsion and the CeO_2 [17, 18]. The increasing the amount of the nanoparticles has a limited effect and from economical side the 50 ppm are best for the smoke reduction.

3.3 Engine performance

BTE is the measure of how efficiently the engine uses from the fuel. Figure 4a shows increasing the load, use of the fuel by the engine increased. Emulsified fuel showed better efficiency of fuel characteristics in compare with net diesel. Nanoparticles effectively increased from the efficiency of the diesel fuel. Cerium dioxide with 150 ppm show 17.23% the higher fuel blend efficiency.

BSFC (brake specific fuel consumption) is the defined kgs of fuel use /brakes power per second. Fuel consumption by the engine increasing at higher load for all net diesel and Nano emulsions. As illustrated in Figure (3b) Nano emulsion have the higher fuel consumed about 4.23% than net diesel, this is due to higher viscosity of the emulsion additional to its lower calorific value against net diesel. This lose in heat can restore by the Cerium dioxide due to the improvement in conductivity of ion oxygen, which enable the fuel to operate at reduced temperature.150 ppm of nanoparticle gave 15.5% the highest fuel consumption.

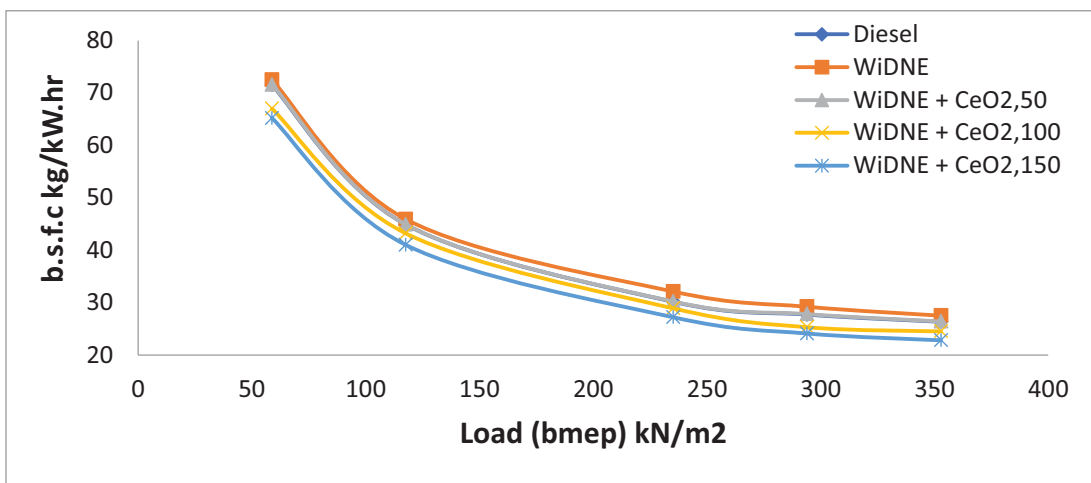


Fig. (3a) Variation of BSFC with Load (bmep) kN/m²

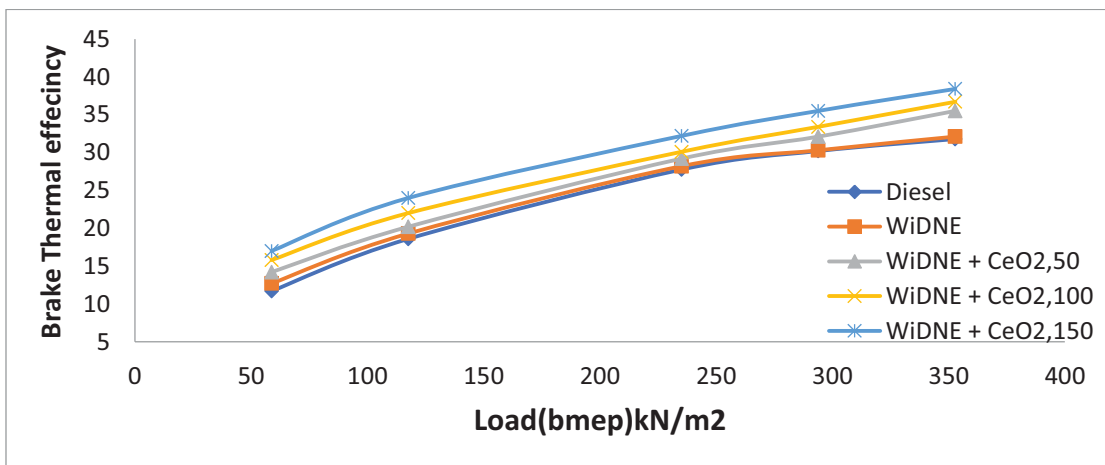


Fig. (3b) Variation of BTE with Load (bmep) kN/m²

4. Conclusion

Preparation of Nano emulsion was achieved successfully due to recording high coefficient of determination R^2 by the RSM at optimization method 98.34%. Suitable contents with the desirability 1.00 for compositions in preparation of emulsified diesel assist to produce a new fuel with a least emissions and higher efficiency.

Presence of water 12% in Nano emulsion contribute effectively in reduction of Smoke opacity to 17.18%, 5.35% NO_x emission and accompanied with higher HC and CO 4.1% and 4.34% respectively.

Use of 150 ppm of CeO₂ dispersed in Nano emulsion assist in enhance the properties of prepared fuel and compensation from the loss in of fuel consumption by providing higher thermal efficiency. 40.6% NO_x, 19.7% CO and 12.85% HC emissions are reduced at higher load. Thermal efficiency and BSFC of new blend fuel are improved 17.23 and 13.4% respectively.

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