

## Development of Alternative Solutions to Reduce Exhaust Emissions in Diesel Engines

Kadir AYDIN\*<sup>1</sup>, Havva Hande ŞAHİN<sup>1</sup>

<sup>1</sup>Çukurova Üniversitesi, Mühendislik Mimarlık Fakültesi, Makine Mühendisliği Bölümü, Adana

Geliş tarihi: 30.01.2017

Kabul tarihi: 19.12.2017

### Abstract

Diesel engines have an important role in environmental pollution. Unfortunately, the fossil fuel combustion comes with both global emissions (CO<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub>), which cause climate change, and local emissions (PM, NO<sub>x</sub>, HC, CO, O<sub>3</sub>), which cause adverse health effects and damage natural environment. The aim of this study is to reduce the level of exhaust emissions by adding fuel additive metal oxide based nanoparticles as an alternative way. In addition, the effect of reducing NO<sub>x</sub> emissions by changing the amount of Adblue sprayed and adding 3% and 5% ammonium sulfate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> to the Adblue solution in the SCR system was investigated. Finally, the optimum addition dosages were determined and exhaust emission values namely NO<sub>x</sub> and CO were reduced with the addition of nanoparticles.

**Keywords:** Heavy duty engines, Nanoparticles, Emissions

## Dizel Motorlarda Egzoz Emisyonlarını Azaltmaya Yönelik Alternatif Çözümlerin Geliştirilmesi

### Özet

Dizel motorların çevre kirliliğindeki rolü çok büyüktür. Ne yazık ki, fosil yakıtların yakılması hem iklim değişikliğine yol açan global emisyonları (CO<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub>), hem de sağlık açısından olumsuz etkilere sahip olan ve doğal çevreye zarar veren bölgesel emisyonları (PM, NO<sub>x</sub>, HC, CO, O<sub>3</sub>), beraberinde getirmektedir. Bu çalışmanın amacı emisyon seviyelerini düşürmek için alternatif bir yol olarak yakıtlara metal oksit esaslı nano partikül katkı maddesi ilave etmektir. Ayrıca SCR sisteminde püskürtülen üre çözeltisi miktarı değiştirilerek ve üre çözeltisine %3 ve %5 oranlarında amonyum sülfat (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> eklenerek NO<sub>x</sub> emisyonlarını azaltma etkisi incelenmiştir. Elde edilen neticeler sonrasında egzoz emisyonlarını azaltmak için uygun katkı dozaj miktarı tespit edilmiş olup kullanılan nanopartikül katkılarının NO<sub>x</sub> ve CO gibi zararlı egzoz emisyon değerlerini azalttığı belirlenmiştir.

**Anahtar Kelimeler:** Ağır vasıta motorlar, Nanopartiküller, Emisyon

---

\*Sorumlu yazar (Corresponding author): Kadir AYDIN, [kdraydin@cu.edu.tr](mailto:kdraydin@cu.edu.tr)

## **1. INTRODUCTION**

Future emission regulations like Euro 5 and presumably Euro 6 will force diesel engine manufacturers to drastically reduce NO<sub>x</sub> and particulate matter (PM) emissions. Although after treatment devices will certainly see great improvements in the future, new in-cylinder strategies are emerging to reduce both NO<sub>x</sub> and PM emissions. External exhaust gas recirculation (EGR) is a well-known in-cylinder method to reduce NO<sub>x</sub> emissions, particularly on modern direct injection (DI) automotive diesel engine, and offers the possibility to decrease temperature during combustion [1,2].

The increase of soot formation with EGR results in an increase of the flame radiation, and thus in a decrease of the flame temperature [3,4]. The premixed part of combustion is higher; without EGR, it may increase NO<sub>x</sub> emissions [4]. However, in the presence of EGR, the rate of heat release (ROHR) premixed peak is lower, so that it would reduce NO<sub>x</sub> emissions [3].

More generally, all the combustion process is delayed with diluted air ID, premixed combustion (diffusion and late diffusion combustion). Consequently, the whole combustion process is shifted further into the expansion stroke, leading to lower combustion temperatures [5]. On the other hand, although modern automotive diesel engines are equipped with an EGR cooler, the inlet air temperature after mixing with recirculated gases increases with EGR ratio, thus reducing the inlet gas density (at constant boost pressure) and in-cylinder trapped mass (thermal throttling). This temperature increase tends to increase NO<sub>x</sub> emissions.

New combustion concepts based on the use of EGR have been studied in order to obtain a dramatic reduction in NO<sub>x</sub> and PM emissions, such as homogeneous charge compression ignition (HCCI) or the low-temperature combustion (LTC). This latter consists generally in utilizing a large amount of EGR. This new combustion concept was first observed by Akihama and co-workers [6] with the so called 'smokeless rich diesel

combustion' obtained with high EGR rates: the smoke suppression, even in rich conditions, is realized by the combustion taking place at temperatures below that needed to form soot. In their modulated kinetics (MK) combustion concept, Kimura and co-workers [7] succeeded in reducing NO<sub>x</sub> and smoke simultaneously through LTC and premixed combustion, without increasing fuel consumption. The MK concept consists in reducing the oxygen concentration with high EGR rates (for the NO<sub>x</sub> reduction) and in prolonging the ID and promoting the dispersion of the injected fuel to accomplish premixed combustion (near HCCI, but not fully homogeneous and combustion is controlled by injection). Another LTC concept named diesel emission at the low limit (DEAL) was patented by Istituto Motori [8].

Selective catalytic reduction (SCR) of NO<sub>x</sub> by nitrogen compounds, such as ammonia or urea commonly referred to as simply "SCR" has been developed for and well proven in industrial stationary applications. The SCR technology was first applied in thermal power plants in Japan in the late 1970s, followed by widespread application in Europe since the mid-1980s. In the USA, SCR systems were introduced for gas turbines in the 1990s, with increasing potential for NO<sub>x</sub> control from coal-fired power plants. In addition to coal-fired cogeneration plants and gas turbines, SCR applications also include plant and refinery heaters and boilers in the chemical processing industry, furnaces, coke ovens, as well as municipal waste plants and incinerators. The list of fuels used in these applications includes industrial gases, natural gas, crude oil, light or heavy oil, and pulverized coal [9].

The application of SCR for mobile diesel engines requires overcoming several problems, which are discussed later. However, SCR remains the only proven catalyst technology capable of reducing diesel NO<sub>x</sub> emissions to levels required by a number of future emission standards. Urea-SCR has been selected by a number of manufacturers as the technology of choice for meeting the Euro V (2008) and the JP 2005 NO<sub>x</sub> limits both equal to 2 g/kWh for heavy-duty truck and bus engines. First commercial diesel truck applications were

launched in 2004 by Nissan Diesel in Japan [10] and by Daimler Chrysler in Europe.

SCR systems are also being developed in the USA in the context of the 2010 NO<sub>x</sub> limit of 0,2 g/bHp-hr for heavy-duty engines, as well as the Tier 2 NO<sub>x</sub> standards for light-duty vehicles. However, the US clean air authorities have voiced concerns about the SCR technology. From the regulatory perspective SCR poses enforcement problems, both in terms of ensuring that the reductant (urea) is available together with diesel fuel throughout the nationwide distribution network, and that it is always timely replenished by vehicle operators.

This paper covers the fundamentals of SCR reductants, chemical reactions, and catalysts as well as stationary SCR systems.

## 2. PREVIOUS WORKS

A detailed analysis of previous and current results of EGR effects on the emissions and performance of diesel engines, spark ignition engines and dual fuel engines is introduced. From the deep analysis, it was found that adding EGR to the air flow rate to the diesel engine, rather than displacing some of the inlet air, appears to be a more beneficial way of utilizing EGR in diesel engines. This way may allow exhaust NO<sub>x</sub> emissions to be reduced substantially. In spark ignition engines, substantial reductions in NO concentrations are achieved with 10% to 25% EGR. However, EGR also reduces the combustion rate, which makes stable combustion more difficult to achieve. At constant burn duration and brake mean effective pressure, the brake specific fuel consumption decreases with increasing EGR. The improvement in fuel consumption with increasing EGR is due to three factors: firstly, reduced pumping work; secondly, reduced heat loss to the cylinder walls; and thirdly, a reduction in the degree of dissociation in the high temperature burned gases. In dual fuel engines, with hot EGR, the thermal efficiency is improved due to increased intake charge temperatures and reburning of the unburned fuel in the recirculated gas. Simultaneously, NO<sub>x</sub> is reduced and smoke is reduced to almost zero at high natural gas

fractions. Cooled EGR gives lower thermal efficiency than hot EGR but makes possible lower NO<sub>x</sub> emissions. The use of EGR is, therefore, believed to be most effective in improving exhaust emissions.

Among the engine after treatment devices, a urea selective catalytic reduction (SCR) is one of the promising after treatment devices for the abatement of exhaust emissions, particularly for NO<sub>x</sub> pollutants. Relative to other alternative after treatment systems, the use of an SCR system can improve the economy of the engine together with the reduction of NO<sub>x</sub> emissions. A compact urea-SCR system reduced more than 70% NO<sub>x</sub> when evaluated on the European Transient Cycle (ETC) and European Steady state Cycle (ESC) [5]. Koebel, Madia and Elsener [4] studied that the urea-SCR system is mounted in the tailpipe of the engine, and consists mainly of coated ceramic converter of honeycomb type and an injector to inject the urea solution. The basic principal of SCR systems is to reduce the NO<sub>x</sub> pollutants by ammonia formed from a urea (32,5 wt%) and water solution called AdBlue.

Berner et al. [11] concluded that a number of studies have demonstrated the control of NO<sub>x</sub> pollutants emitted from diesel engines with the use of a urea-SCR aftertreatment system, and the reduction of unregulated chemical species have also been reported with these systems. However, unregulated emissions such as particles number-size distribution, volatile organic compounds (VOC)-components and carbonyl compounds (CC) still need to be addressed in detail. The present study focused on the investigation of the effectiveness of vanadium based urea-SCR catalyst employed in a diesel engine, in terms of number size distribution of particles emissions, and conversion efficiency of carbonyls and VOC's emitted in the engine exhaust.

To our knowledge, there are no studies published on the influence of urea on the evaporation of water from a UWS droplet. Van Helden, Verbeek and Willems [12] used water instead of UWS in a CFD study and estimated the concentration of the reducing agent from the water vapour

concentration of the reducing agent from the water vapour concentration.

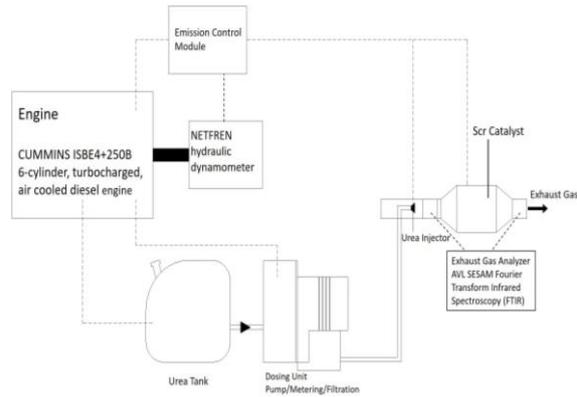
### 3. MATERIAL VE METHOD

The aim of this work is to review the potential of exhaust gas recirculation (EGR) and to find out the alternative way of the engine after treatment system to obtain the same emission limit, particularly NO<sub>x</sub> emissions, and to reduce the exhaust emissions. There are many ways to obtain the same exhaust emission limit. Experimental setup is established in Automotive Engineering Research Laboratory of Çukurova University. Commercially available diesel engine is fitted with SCR exhaust emission treatment system. The effect of urea injection pressure, amount of the urea, SCR catalyst efficiency, effects of the amount of EGR, temperatures of EGR, alternatives to the EGR, alternative catalysts for the reduction of HC, CO, PM and alternative chemicals for the reduction of NO<sub>x</sub> will be investigated.

In this study, 4 stroke, 4 cylinders turbocharged and intercooled Cummins ISBe4+250 type engine with Euro 4 exhaust gas treatment system was used for the engine set up. This engine has Euro 4 OBD Stage 1 emission limit with NO<sub>x</sub> control. Advertised power of this engine equals to 184 kW at 2500 rpm and the peak torque 1020 Nm at 1500 rpm. Engine torque and brake power is measured by a fully automated hydraulic dynamometer (Netfren) with the torque interval of 250-2200 Nm and engine speed interval of 0-4500 rpm. A schematic diagram of experimental unit is shown in Figure 1.

The concentrations of the gas emissions were measured by employing an AVL Sesam i60 FT Fourier Transform Infrared Spectroscopy (FTIR) multi-component exhaust analyser, and the test range accuracy for all types of exhaust emission are less than 0,01. The FTIR was calibrated to detect CO, CO<sub>2</sub>, NO, NO<sub>2</sub>, NO<sub>x</sub>, N<sub>2</sub>O, NH<sub>3</sub>, CH<sub>4</sub>, SO<sub>2</sub> and other pollutants. Among all detected compounds by FTIR. For the determining exhaust emissions limit of European Union, hydrocarbons (HC), carbon monoxide (CO), oxides of nitrogen

(NO<sub>x</sub>) and particulate matter (PM) are have to be measured together. HC, CO, NO<sub>x</sub> and PM were also be measured by MRU Delta 1600V type portable emission measurement system. Both measured NO<sub>x</sub> values using two different types of exhaust gas analyser have to be increased the sensitivity of measurement.



**Figure 1.** The schematic diagram of the experimental unit

Six different nanoparticles namely titanium oxide, iron oxide, zinc oxide, magnesium oxide, nickel oxide and silicon oxide and that particle sizes ranging between 10-50 nanometer and commercially availed were used as fuel additive. Properties of these nanoparticles specified in Table 1. Additives of nanoparticles were supplement 15, 20 and 25 ppm doses in weight basis. The amount of nanoparticles that are required for all level of doses were measured using electronic precision scales with sensitivity of 0,0001 g. Nanoparticle additives in order to provide a homogeneous mixture are mixed with diesel fuel using ultrasonic mixer during half an hour to prepare test fuels. These test fuels were used in order to prevent any precipitation without delay.

**Table 1.** Properties of nanoparticles used in the experimental tests

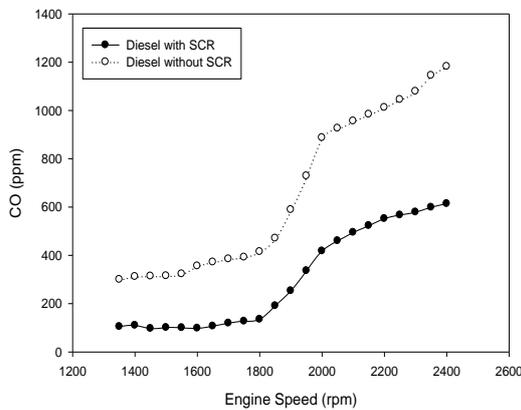
Nanoparticle	Symbol	P. Size (nm)	Purity (%)
Titanium Oxide	TiO <sub>2</sub>	10-50	99.9
Iron Oxide	Fe <sub>2</sub> O <sub>3</sub>	30	99.99
Magnesium Oxide	MgO	30	99.9
Zinc Oxide	ZnO	50	99.9
Nickel Oxide	NiO	30	99.9
Silicon Oxide	SiO <sub>2</sub>	<30	99.99

Sonic Vibra-Cell VC750 model ultrasonic processor was used to mix nanoparticles with diesel fuel homogeneously so as to acquire blend fuels. Nanoparticles were mixed with diesel and by pulsing time 10 seconds on 10 seconds off and 40% amplitude by means of ultrasonic processor.

All experimental tests were performed three times to reduce experimental errors. Average values of experimental results were used for the plotting graphs.

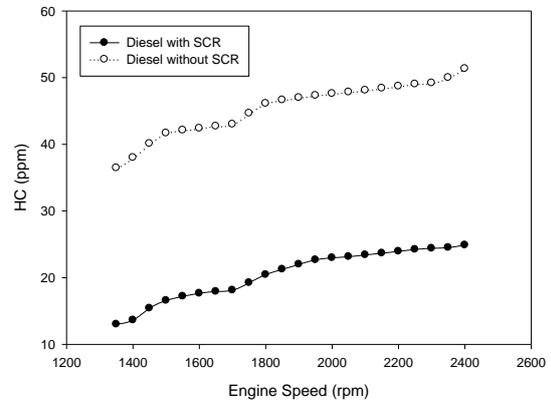
#### 4. RESULTS AND DISCUSSIONS

The engine used in the experimental study is equipped exhaust gas after treatment system. SCR system is the key equipment of engine exhaust gas after treatment system. The efficiency of SCR system is tested to measure the reduction rates of CO, HC and NO<sub>x</sub> emissions. The carbon monoxide (CO) emissions of diesel fuel as a function of engine speed with and without SCR is illustrated in figure 2. It indicates that the average reduction in CO emission value is 58.4% with SCR system compared to diesel fuel without SCR system.



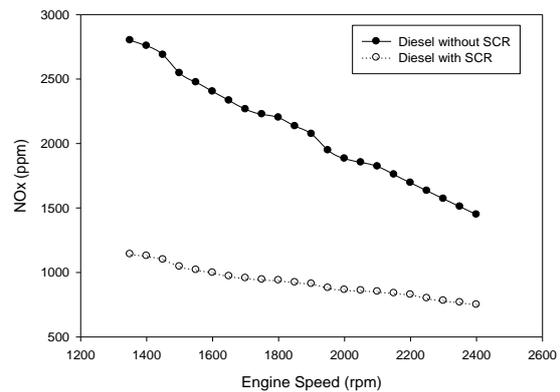
**Figure 2.** CO emission values of diesel fuel with and without SCR system

The results of measured HC emission values of diesel fuel with and without SCR system for different engine speeds at full load condition was represented in Figure 3. It is observed that the average HC reduction is 56.5%.



**Figure 3.** HC emission values of diesel fuel with and without SCR system

Figure 4 presents the NO<sub>x</sub> emission values of diesel fuel with and without SCR system. The results showed that the average NO<sub>x</sub> reduction obtained from experimental result is 42.6%.



**Figure 4.** NO<sub>x</sub> emission values of diesel fuel with and without SCR system

The exhaust emission test on the Euro 4 engine are performed on the existing system, after testing of the existing system, the system to be developed by adding 15, 20 and 25 ppm nanoparticles (zinc oxide, nickel oxide, magnesium oxide, titanium dioxide, nickel ferrous oxide, silicon oxide, aluminium oxide, the alloy of the combination of zinc oxide, nickel oxide, and ferrous oxide) to the fuel. The exhaust gases released after the oxidation and combustion of the fuel are measured and it will be checked according to Euro 5 and Euro 6 emission criteria.

After starting to use of Euro 4 emission standards diesel fuel is mixture with Adblue (32.5 wt% urea and 67.5 wt% water solutions) and then this mixture is taken to the cylinder for combustion. Used Adblue ratio is increased by renewed emission standard because of decrease in emissions. Adblue mixing ratio is 3-4% in Euro 4 and 5-7% in Euro 5. Table 2 illustrates the effects of exhaust emissions with respect to 5% Adblue addition into testing fuel.

**Table 2.** Effects of 5% Adblue addition to diesel fuel on exhaust emissions

RPM	NOx (5% AdBlue)	CO (5% AdBlue)	CO <sub>2</sub> (5% AdBlue)	HC (5% AdBlue)
1200	↓ -5.79%	↓ -2.02%	↑ 3.05%	↓ -17.46%
1400	↓ -2.30%	↓ -2.55%	↑ 3.30%	↓ -4.89%
1600	↓ -1.39%	↓ -3.76%	↑ 5.93%	↓ -2.24%
1800	↓ -1.71%	↓ -1.87%	↑ 5.83%	↓ -2.13%
2000	↓ -4.26%	↓ -9.26%	↑ 6.20%	↓ -3.58%
2200	↓ -13.03%	↓ -1.79%	↑ 7.07%	↓ -2.29%

Addition to 5% Adblue to pure diesel leads to 4.74% average decrease in NO<sub>x</sub> emission, 3.54% average decrease in CO emission, 5.23% average increase in CO<sub>2</sub> emission and 5.43% average decrease in HC emission is observed compared to pure diesel.

It is evaluated that adding 3% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> to the urea, the NO<sub>x</sub> emission level is decreased. Unburned NH<sub>4</sub><sup>+</sup> entered into reaction and revealed additional NO<sub>x</sub> through the agency of addition of 3% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> salt to the urea. Urea is mixed up diesel and the amount of injected urea must match the ammonia demand corresponding to the amount of NO<sub>x</sub> entering the catalyst and the NO<sub>x</sub> conversion efficiency at given operating conditions (catalyst temperature and space velocity).

Table 3 illustrates the percentage of exhaust emission with respect to 3% addition to (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> to the urea. NO<sub>x</sub> emission is decreased by addition ammonium sulphate salt to urea solution. The maximum reduction of NO<sub>x</sub> emission is 17.69% at 2200 rpm for 3% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> addition to Adblue (urea solution). The average reduction of CO emission is 4.44% and the average reduction of HC emission is 6.29% for 3% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> addition to urea solution respectively.

**Table 3.** Effects of ammonium sulphate salts addition to urea on exhaust emissions

RPM	NOx (3% (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> )	CO (3% (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> )	CO <sub>2</sub> (3% (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> )	HC (3% (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> )
1200	↓ -16.70%	↓ -2.77%	↑ 21.52%	↓ -17.46%
1400	↓ -9.29%	↓ -2.06%	↑ 16.86%	↓ 2.70%
1600	↓ -7.88%	↓ -1.59%	↑ 14.43%	↓ -1.87%
1800	↓ -3.55%	↓ -5.10%	↑ 9.54%	↓ -2.82%
2000	↓ -11.52%	↓ -6.98%	↑ 12.80%	↓ -4.86%
2200	↓ -17.69%	↓ -8.13%	↑ 5.34%	↓ -13.45%

The diesel fuel with nanoparticle additive is found to have decreasing trend of NO<sub>x</sub> emission from the conventional diesel operation. Table 4 shows the effects of 15, 20, 25 ppm MgO additions to the diesel fuel for the exhaust emissions reduction.

**Table 4.** Effects of percent dosages of MgO addition to the diesel fuel on exhaust emissions

RPM	NOx (MgO 15 ppm)	CO (MgO 15 ppm)	CO <sub>2</sub> (MgO 15 ppm)	HC (MgO 15 ppm)
1200	↓ -9.54%	↓ -7.81%	↑ 2.75%	↓ -3.83%
1400	↓ -9.04%	↓ -4.51%	↑ 3.26%	↓ -3.11%
1600	↓ -3.86%	↓ -12.17%	↑ 5.04%	↓ -5.57%
1800	↓ -2.31%	↓ -12.24%	↑ 6.75%	↓ -3.31%
2000	↓ -13.93%	↓ -9.45%	↑ 5.42%	↓ -5.74%
2200	↓ -24.56%	↑ 4.26%	↑ 4.94%	↓ -3.27%

RPM	NOx (MgO 20 ppm)	CO (MgO 20 ppm)	CO <sub>2</sub> (MgO 20 ppm)	HC (MgO 20 ppm)
1200	↓ -1.36%	↓ -2.52%	↑ 6.51%	↓ -7.42%
1400	↑ 9.94%	↓ -3.24%	↑ 7.47%	↑ 0.86%
1600	↓ -8.99%	↓ -14.75%	↑ 6.69%	↑ 6.76%
1800	↓ -3.62%	↓ -16.39%	↑ 11.03%	↓ -5.28%
2000	↓ -11.73%	↓ -13.47%	↑ 9.31%	↓ -12.94%
2200	↓ -25.22%	↑ 0.29%	↑ 9.35%	↓ -12.54%

RPM	NOx (MgO 25 ppm)	CO (MgO 25 ppm)	CO <sub>2</sub> (MgO 25 ppm)	HC (MgO 25 ppm)
1200	↓ -15.27%	↓ -11.59%	↑ 9.25%	↓ -20.10%
1400	↓ -2.88%	↓ -8.54%	↑ 9.53%	↓ -1.54%
1600	↓ -8.42%	↓ -15.98%	↑ 14.81%	↓ -7.36%
1800	↓ -4.79%	↓ -23.41%	↑ 15.87%	↓ -4.74%
2000	↓ -25.41%	↓ -12.98%	↑ 18.12%	↓ -12.94%
2200	↓ -30.17%	↓ -7.88%	↑ 19.31%	↓ -12.56%

15, 20, 25 ppm dosages of MgO additive caused a decrease in NO<sub>x</sub>, CO and HC emissions. The average NO<sub>x</sub> emissions decrease of 10.54%, 6.83%, 14.49%, average CO emissions decrease of 6.99%, 8.35%, 13.40% and similarly the average HC emissions decrease of 4.14%, 5.09%, 9.87% are observed with respect to 15, 20, 25 ppm MgO nanoparticles addition to the diesel fuel. Nanoparticles make the combustion more complete by oxygen supplementation to the cylinder. This situation causes decrease in CO emission of exhaust gases.

Table 5 illustrates the effects of 15, 20, 25 ppm TiO<sub>2</sub> additions to the diesel fuel for the exhaust emissions reduction.

**Table 5.** Effects of percent dosages of TiO<sub>2</sub> addition to the diesel fuel on exhaust emissions

RPM	NO <sub>x</sub> (TiO <sub>2</sub> 15 ppm)	CO (TiO <sub>2</sub> 15 ppm)	CO <sub>2</sub> (TiO <sub>2</sub> 15 ppm)	HC (TiO <sub>2</sub> 15 ppm)
1200	-15.20%	-2.02%	1.34%	-13.40%
1400	-12.24%	-4.32%	2.92%	-1.46%
1600	-4.78%	-1.09%	5.17%	-3.88%
1800	-5.31%	-7.17%	1.91%	-1.44%
2000	-21.99%	-9.42%	4.23%	-2.24%
2200	-24.80%	-14.22%	3.41%	-1.67%
RPM	NO <sub>x</sub> (TiO <sub>2</sub> 20 ppm)	CO (TiO <sub>2</sub> 20 ppm)	CO <sub>2</sub> (TiO <sub>2</sub> 20 ppm)	HC (TiO <sub>2</sub> 20 ppm)
1200	-12.27%	-2.90%	2.61%	-16.03%
1400	-12.57%	-6.58%	4.78%	-3.21%
1600	-8.91%	-4.29%	6.30%	-4.66%
1800	-5.69%	-9.36%	4.02%	-1.59%
2000	-21.78%	-12.28%	6.64%	-3.91%
2200	-25.17%	-17.74%	6.98%	-2.99%
RPM	NO <sub>x</sub> (TiO <sub>2</sub> 25 ppm)	CO (TiO <sub>2</sub> 25 ppm)	CO <sub>2</sub> (TiO <sub>2</sub> 25 ppm)	HC (TiO <sub>2</sub> 25 ppm)
1200	-12.95%	-4.03%	3.82%	-18.18%
1400	-9.37%	-7.46%	7.18%	-6.65%
1600	-7.91%	-7.00%	9.07%	-7.77%
1800	-6.25%	-11.90%	5.83%	-2.57%
2000	-34.47%	-14.04%	7.31%	-4.13%
2200	-51.32%	-18.48%	9.02%	-5.69%

15, 20, 25 ppm dosages of TiO<sub>2</sub> additive caused a decrease in NO<sub>x</sub>, CO and HC emissions. The average NO<sub>x</sub> emissions decrease of 14.05%, 14.40%, 20.38%, average CO emissions decrease of 6.37%, 8.86%, 10.49%, and similarly the average HC emissions decrease of 4.02%, 5.40%, 7.50% are observed with respect to 15, 20, 25 ppm TiO<sub>2</sub> nanoparticles addition to the diesel fuel.

Table 6 shows the effects of 15, 20, 25 ppm ZnO additions to the diesel fuel for the exhaust emissions reduction.

**Table 6.** Effects of percent dosages of ZnO addition to the diesel fuel on exhaust emissions

RPM	NO <sub>x</sub> (ZnO 15 ppm)	CO (ZnO 15 ppm)	CO <sub>2</sub> (ZnO 15 ppm)	HC (ZnO 15 ppm)
1200	-9.20%	-2.02%	1.34%	-2.15%
1400	-9.29%	-0.98%	1.75%	-0.81%
1600	-3.75%	-3.19%	1.23%	-2.24%
1800	-3.08%	-7.06%	2.06%	-0.45%
2000	-12.87%	-9.45%	4.23%	-1.06%
2200	-22.95%	-2.79%	3.44%	-2.67%
RPM	NO <sub>x</sub> (ZnO 20 ppm)	CO (ZnO 20 ppm)	CO <sub>2</sub> (ZnO 20 ppm)	HC (ZnO 20 ppm)
1200	-9.75%	-3.65%	2.70%	-4.78%
1400	-13.89%	-2.06%	2.98%	-3.78%
1600	-6.63%	-10.69%	4.58%	-5.62%
1800	-7.67%	-10.63%	2.88%	-1.44%
2000	-16.14%	-13.76%	8.19%	-2.24%
2200	-36.03%	-7.59%	4.97%	-3.02%
RPM	NO <sub>x</sub> (ZnO 25 ppm)	CO (ZnO 25 ppm)	CO <sub>2</sub> (ZnO 25 ppm)	HC (ZnO 25 ppm)
1200	-14.11%	-5.04%	4.08%	-9.81%
1400	-16.60%	-5.59%	4.82%	-6.65%
1600	-6.83%	-12.90%	5.93%	-7.26%
1800	-9.75%	-13.39%	4.52%	-2.77%
2000	-24.46%	-18.77%	10.25%	-3.91%
2200	-36.43%	-11.50%	6.05%	-3.63%

15, 20, 25 ppm dosages of ZnO additive caused a decrease in NO<sub>x</sub>, CO and HC emissions. The average NO<sub>x</sub> emissions decrease of 10.19%, 15.02%, 18.03%, average CO emissions decrease of 4.25%, 8.06%, 11.20%, and similarly the average HC emissions decrease of 1.56%, 3.48%, 5.67% are observed with respect to 15, 20, 25 ppm ZnO nanoparticles addition to the diesel fuel.

## 5. CONCLUSIONS

Transport is crucial for economic and social development of a society as it serves a key role for transportation of goods and people. But it is not free of negative externalities. Operation of transport vehicles require energy use and this energy is mostly generated with fossil fuel combustion. Unfortunately, the fossil fuel combustion comes with both global emissions (CO<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub>), which cause climate change, and local emissions (PM, NO<sub>x</sub>, HC, CO, O<sub>3</sub>), which cause adverse health effects and damage natural environment.

In general, compared to common diesel engine, there is a reduction of NO<sub>x</sub> emission when the engine is fuelled with ammonium-sulphate salts, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> may be formed on the catalyst surface at the low temperatures, the involved ammonium ions can react easily with NO under the reaction conditions, which avoids deposition of excess ammonium-sulphate salts on the catalyst surface and thus the catalyst deactivation. A small amount of ammonium-sulphate salts deposits on the surface of the catalyst, which promote the SCR activity. The results showed that addition various rates ammonium sulphate salts to urea solution increases the NO<sub>x</sub>, CO and HC conversion ratio.

The maximum average NO<sub>x</sub> emission reduction was obtained with TiO<sub>2</sub> nanoparticle at the addition dosage of 25 ppm as 20.38%. NO<sub>x</sub> emission is reduced due to complete combustion of oxygenated fuel blends with the help of catalyst impact of nanoparticle additions which advances heat transfer in the combustion chamber owing to nanoparticle additives metallic base structures.

The reason of the carbon monoxide emission is incomplete combustion, which is raised by a lack of oxidants, residence time and temperature. The CO emissions decrease slightly with the use of nanoparticule additives. This may be owing to catalytic activity of nanoparticules and improving the fuel-air mixing in the combustion chamber, and in turn resulting reduced CO emissions. The reduction of CO emissions observed are 10.49%, 13.40% and 11.20% at 25 ppm dosage for TiO<sub>2</sub>, MgO and ZnO at full load respectively.

HC emissions contribute to the formation of smog and may include photochemically reactive species as well as carcinogens. Fuel-lean combustion at full load leads to a drop of 9.87%, 7.50% and 5.67% in hydrocarbon emission with 25 ppm MgO, TiO<sub>2</sub> and ZnO nanofuels respectively. Reduction in HC emissions may be due to secondary atomization, shorten ignition delay, and catalytic activity of nanoparticule additives leading to better combustion.

25 ppm metal based nanoparticules addition to the diesel fuel increase the reaction rates of exhaust after treatment system because of their effects on increased heat transfer ratio. 25 ppm ZnO, TiO<sub>2</sub> and MgO metal nanoparticles addition to the diesel fuel are determined as the most proper additives for emission reductions. More details about the emission reduction effects of metal based nanoparticules addition into the diesel fuel can be found in references 13,14 and 15.

## REFERENCES

1. Cho, S.M., 1994. Properly Apply Selective Catalytic Reduction for NO<sub>x</sub> Removal. *Chem. Eng. Prog.*, 39-45.
2. Cobb, D., Glatch L., Rudd, J., Snyder, S., 1991. Application of Selective Catalytic Reduction (SCR) Technology for NO<sub>x</sub> Reduction from Refinery Combustion Sources. *Environmental Progress*, 10:49-59.
3. Hirata, K., Masaki, N., Ueno, H., Akagawa, H., 2005. Development of Urea-SCR System for a Heavy-Duty Commercial Vehicles. SAE Technical Paper 2005-01-1860.
4. Koebel, M., Madia, G., Elsener, M., 2002. Selective Catalytic Reduction of NO and NO<sub>2</sub> at Low Temperatures. *Catalysis Today*, 73: 239-247.
5. <http://www.eere.energy.gov/vehiclesandfuels/pdfs/deer>
6. Mathes, W., Witzel, F., Schnapp, S., 1999. Exhaust Gas Control System for Diesel Engine Exhaust Gases. International Patent Application, WO 99/05402.
7. <http://www.businessinsider.com/adding-urea-to-clean-diesel-cars-can-i-just-pee-in-the-tank-2011-5#ixzz3XBp2lw3G>
8. Bosch, H., Janssen, F., 1988. Formation and Control of Nitrogen Oxides. *Catal Today*, (2):369.
9. Cobb, D., Glatch, L., Rudd, J., Snyder, S., 1991. Application of Selective Catalytic Reduction (SCR) Technology for NO<sub>x</sub> Reduction from Refinery Combustion Sources. *Environmental Progress*, 10:49-59.
10. Hirata, K., Masaki, N., Ueno, H., Akagawa, H., 2005. Development of Urea-SCR System for a Heavy-Duty Commercial Vehicles. SAE Technical Paper 2005-01-1860.
11. Berner, G., 1993. Static Mixer. International Patent Application, WO 93/00990.
12. Van Helden, R., Verbeek, R., Willems, F., 2004. Optimisation of Urea SCR de NO<sub>x</sub> Systems for HD Diesel Engines. SAE, 2004-01-0154.
13. Ozgur, C., Ozgur, T., Ozcanlı, M., Aydin, K., 2015. Determination of the Impacts of Nanoparticule Additives into Diesel Fuel on NO<sub>x</sub> Emmission Characteristics of a Heavy Duty Diesel Engine, *Applied Mechanics and Materials*, 799:857-860.
14. Ozgur, T., Tuccar, G., Uludamar, E., Yilmaz, A.C., Gungor, C., Ozcanli, M., Serin, H., Aydin, K., 2015. Effect of Nanoparticle Additives on NO<sub>x</sub> Emissions of Diesel Fueled Compression Ignition Engine, *International Journal of Global Warming*, 7:487-498 .
15. Ozgur, T., Ozcanlı, M., Aydin, K., 2015. Investigation of Nanoparticle Additives to Biodiesel for Improvement of the Performance and Exhaust Emissions in a Compression Ignition Engine, *International Journal of Green Energy*, 12:51-56.