# REDUCTION OF HARMFUL NITROGEN OXIDE EMISSION FROM LOW HEAT REJECTION DIESEL ENGINE USING CARBON NANOTUBES

by

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Original scientific paper
DOI: 10.2298/TSCI16S4181T

*In this study, lanthanum aluminate is used as thermal barrier coating material for the first time in the internal combustion engine to convert the standard engine into low heat rejection engine. Initially, the biodiesel is prepared from sunflower oil by using trans-esterification process. The piton crown, cylinder head and valves of the engine is coated with lanthanum aluminate for a thickness of around 200 microns. However, the analysis of performance and emission characteristics of a standard diesel is carried out with diesel/biodiesel to compare with the low heat rejection engine. The lanthanum aluminate coated engine fueled with sunflower methyl ester shows better performance and emission. But the emission of* $NO_x$ *founds to be higher in the coated engine. Further, a small quantity of carbon nanotubes is added onto the biodiesel to carry out the experiments. Based on the results, the carbon nanotubes are added with the biodiesel to reduce the emission of* $NO_x$*.*

Key words: *heat rejection engine, lanthanum aluminate, thermal barrier coating,* $NO_x$*, carbon nanotubes*

## Introduction

As the fossil fuels are continuously depleting and the price of fuels is increasing, there is a need to find an alternate fuel source for the internal combustion engine. One such alternate source is the vegetable oils. If a biodiesel is used in a Diesel engine, there will be reduction in the emission of CO, HC, and smoke due to high availability of oxygen [1, 2]. The utilization of biodiesel as an alternate source has increased in the modern era. But the biodiesels are used without any modifications in the Diesel engine with high proportions due to lack of skill [3]. Apart from this problem, the emission of $NO_x$ form the biodiesel was greater compared to diesel [4].

However, $NO_x$ is very undesirable. Regulations to reduce $NO_x$ emissions continue to become more stringent. The emitted $NO_x$ reacts in the atmosphere to form ozone and it is one of the major causes of photochemical smog. In addition, $NO_x$ is the most dangerous emission from the compression ignition engine. In order to reduce the harmful emissions from the diesel engine, various techniques such as exhaust gas re-circulation have been employed [5]. But the

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technique used to reduce the emission of $NO_x$ will increase the emission of HC, CO, smoke, and *vice versa*. In order to reduce all the emissions such as CO, HC, and $NO_x$, emulsification technique has been adopted. The emulsification of biodiesel with the addition of water showed improvement in the reduction of harmful emissions without affecting the performance characteristics [6-10]. It has been inferred that the ignition delay period has been increased due to the emulsification of fuel as there is reduction in cetane number due to addition of water [11-13].

Nano particles are used to overcome the shortcomings of the emulsified fuel. The nano particles have high surface area and it enables high reactivity. The nano additives in the HC fuels such as diesel and biodiesel could shorten the ignition delay period [14-16]. The carbon nanotubes (CNT) can increase the burning rate of the fuel and it increases the cetane number of the fuel [17]. The CNT have been used as the nano additive in the diesel and biodiesel of sunflower oil in this study. In order to improve the performance and efficiency of the engine, coating of combustion chamber elements with a ceramic material is recommended. The in-combustion temperature of the coated engine is higher compared to uncoated engine [18]. Due to increase in temperature of the combustion chamber, there was a decrease in ignition delay [19, 20]. The materials such as partially stabilized zirconium (PSZ), mullite, and yttrium stabilized zirconium (YSZ) have been used for the coating the engine parts [19, 20]. Till now lanthanum aluminate ($LaAlO_3$) has not been used as the thermal barrier coating material.

The present work focuses on the analysis of performance, emission characteristics of uncoated, and $LaAlO_3$ coated engine with diesel and sunflower methyl ester (SME) B100 (100% SME and 0% diesel). Further, the analysis was again carried out in the coated engine alone with CNT injected SME B100.

## Materials and methods

### *Biodiesel production*

The crude sunflower oil was purchased from Selva Kumaran Oil Stores, Madurai, India. The raw oil was filtered to the remove the impurities and it was heated to the temperature of about 120 °C. Further, the oil was made to undergo base catalyst esterification process. The trans-esterification process method required 17% of methanol by volume and 1% of KOH by weight. The molar ratio maintained was 6:1 [24-26]. Then, the methanol solution was mixed with the heated oil and stirred continuously with the help of the magnetic stirrer. It was allowed to settle and the two distinct layers were formed. The upper layer was the sunflower biodiesel and the lower layer was the glycerin. The yield of biodiesel obtained was about 93% and the synthesized biodiesel were tested to determine the fuel properties. The obtained properties were compared with the properties of diesel.

### *Preparation of CNT blended SME fuel*

The CNT were prepared by electric arc discharge method in College of Engineering, Guindy, India. The average particle size diameter of the prepared CNT was 15 nm. The number of shells in the CNT was two. It was black in color and has 675 $m^2/g$ of specific surface area. The synthesized CNT were to be mixed with already prepared biodiesel and agitated at a speed of about 2500 rpm. It was to be noticed that 100 ppm of CNT was mixed with fuel. The properties of various fuels such as diesel, SME, and CNT blended SME biodiesel is compared in tab. 1.

**Table 1. Fuel properties**

| Properties | Diesel | SME | SME B100 with CNT |
|---|---|---|---|
| Kinetic viscosity [cSt] | 3.08 | 5.3 | 6.01 |
| Density at 15 °C [$kgm^{-3}$] | 848 | 886 | 891 |
| Cetane number | 45 | 51 | 54 |
| Calorific value [$MJkg^{-1}$] | 42.6 | 40.13 | 39.74 |
| Flash point [°C] | 57 | 90 | 126 |
| Fire point [°C] | 64 | 116 | 150 |

### *Thermal barrier coating of engine components*

Earlier reports based on investigations of PSZ and YSZ as the thermal barrier coating materials are available in higher dimension. However, there is no investigation available regarding $LaAlO_3$ as the coating material. The comparison of various properties of the $LaAlO_3$ with various thermal barrier coating materials have been presented in tab. 2. The $LaAlO_3$ coated in the combustion chamber elements such as piston crown, inlet valves, outlet valves, and cylinder head was purchased from Premnath Eshwar Scientific Company, Salem, India. The coating technique selected for converting the STD engine into the low heat rejection engine was plasma spraying process. The coating thickness employed was about 200 microns.

**Table 2. Properties of various thermal barrier coatings**

| Properties | 7-8% YSZ | $CeO_2$ | Mullite | $Al_2O_3$ + 40% $ZrO_2$ | $BaZrO_3$ | $LaAlO_3$ |
|---|---|---|---|---|---|---|
| Thermal conductivity [$Wm^{-1}K^{-1}$] | 1 | 2.77 | 3.3 | 8 | 3.42 | 1.7 |
| Thermal expansion coefficient [$(1\ k^{-1})\cdot10^{-6}$] | 10.9 | 13 | 5.3 | 7.5 | 8.1 | 10.1 |
| Density [$kgm^{-3}$] | 5650 | 5253 | 4550 | 4000 | 4200 | 4325 |
| Specific heat [$Jkg^{-1}K^{-1}$] | 620 | 470 | 523 | 825 | 450 | 8.6 |

### *Experimental set-up and procedure*

The experiment was carried out in a 4-stroke, vertical air cooled single cylinder engine. The detailed specifications of the engine are presented in tab. 3. The capacity of the engine was 661 $cm^3$. The fuel injection pressure was maintained at 220 bar throughout the experiment and allowed to reach its steady-state. The STD injection timing was 23° crank angle. The diameter of the cylinder is 87.5 mm and the length of the cylinder is 110 mm. The rated power of the engine is 4.4 kW. The compression ratio of the engine in which the analysis was carried out is 17.5:1.

**Table 3. Specification of the engine**

| Type | 4-stroke, single cylinder vertical air cooled engine |
|---|---|
| Rated power | 4.4 kW |
| Bore diameter [$D$] | 87.5 mm |
| Stroke [$L$] | 110 mm |
| Compression ratio | 17.5:1 |
| Injection pressure | 200 bar |
| Cubic capacity | 661 $cm^3$ |

The engine was coupled with an eddy current dynamometer to apply different engine loads. The AVL 444 di-gas analyzers were used to measure the emissions of CO, HC, and $NO_x$. The exhaust gas temperature was measured using thermocouples. The experimental set-up is shown in fig. 1. The analysis of combustion, performance, emission characteristics of the uncoated/coated engine fueled with diesel, and SME was carried out without any modifications in the engine.

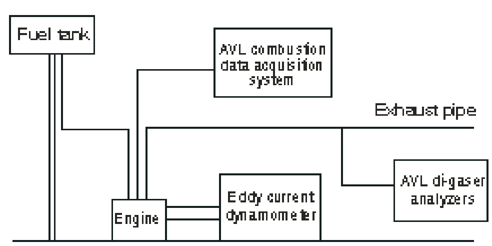


**Figure 1. Experimental set-up**

## Results and discussions

### *Brake thermal efficiency*

Brake thermal efficiency indicates how effectively the heat energy of the fuel is converted into useful work at the crankshaft. The brake thermal efficiency for the coated and uncoated engine has been presented in fig. 2. It is clear that the brake thermal efficiency varies lin-

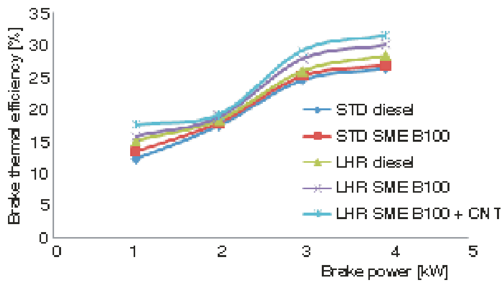


**Figure 2. Comparison of brake thermal efficiency**

early with the load. The brake thermal efficiency is higher for the coated engine than the uncoated engine for both the fuels such as diesel and pure SME. The efficiency of engine when operated with SME B100 is greater than that of operated with the diesel.

It is observed that the brake thermal efficiency increased by 11.57% for the SME B100 and 7.7% for the diesel in the coated engine when compared with the uncoated engine at the full load condition. This is due to the decreasing in-cylinder heat transfer in the coated engine. The coated engine fueled CNT injected SME biodiesel showed highest efficiency. It was found that there was 19.9% increase in brake thermal efficiency when CNT was added with the biodiesel in the coated engine.

*Brake specific fuel consumption*

The brake specific fuel consumption indicates the amount of fuel consumed per unit time to develop unit power. It is an important parameter that indicates how well the performance of the engine is. It is inversely to the thermal efficiency of the engine. The comparison of brake specific fuel consumption for the coated and uncoated engine is shown in fig. 3.

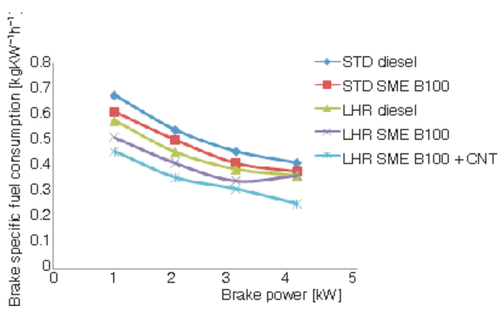


**Figure 3. Comparison of brake specific fuel consumption**

The specific fuel consumption decreases with increase in the load. The fuel consumption for the lanthanum zirconate coated engine is found to be lower than the uncoated engine. It was found that the fuel consumption of the coated engine is lower by 17.8% for SME B100 and 19% lower for the diesel than in the uncoated engine. The main reason for the decreased fuel consumption is increase in temperature of the cylinder wall which again leads to decrease in ignition delay period of the fuel which has the positive effect on physical and chemical properties of the fuel. When the CNT was mixed with the biodiesel in the coated engine, the fuel consumption was decreased further.

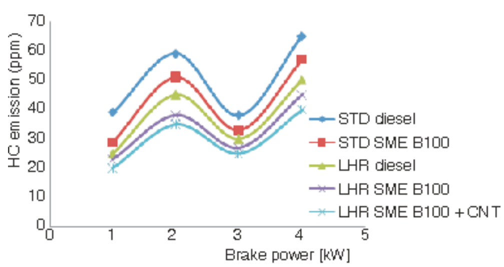


**Figure 4. Emission comparison of unburnt HC**

*Emission of unburnt hydrocarbons*

The unburnt HC emissions are the result of incomplete combustion. The parameters that have an influence over the emission of HC are the air-fuel ratio, combustion chamber design, and load applied on the engine. The variation in the emission of HC with respect to the brake power is shown in fig. 4. The coated engine has lower HC emission than that of the uncoated engine. The emission of HC was found to be lower in the coated engine by 38.4% for diesel and 38.5% for SME B100 at the full load condition. The main reason for the decrease in HC emission in the coated engine is that increased combustion duration which leads to complete combustion of the fuel. The $LaAlO_3$ coated engine operated with the SME B100 has the lowest HC emission at all the load conditions. Further, decrease of about 38.46% was found when CNT was added in the biodiesel in the $LaAlO_3$ coated engine than the standard engine operated with diesel.

### *Carbon monoxide emission*

The emission of CO is due to low oxygen content in the air fuel mixture. The CO would be present in the air-fuel mixture below 16:1. But in actual practice, it could not be neglected even in the lean mixtures. The emission of CO with respect to the brake power for both the coated and uncoated engines fueled with diesel and SME B100 has been presented in fig. 5. From fig. 5, it is clear that the CO emission is found to be lower in the coated engine than the uncoated engine. It is found that the CO emission was lower in the coated engine by 33.33% when diesel was used as the test fuel and 28.57% when SME was used as the test fuel when compared with the uncoated engine. The main reason for the decreased emission of CO in the coated engine into $CO_2$. Overall the CNT injected biodiesel in the coated engine showed least emission of CO.

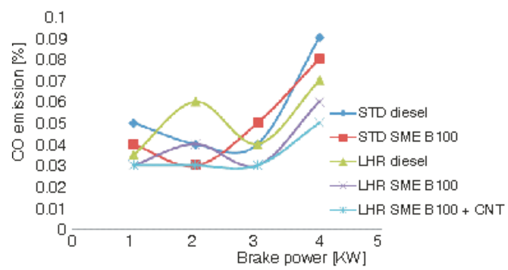

**Figure 5. Emission comparison of CO**

### *Emission of $NO_x$*

The $NO_x$ is the most harmful emission form the engine exhaust. The causes for the emission of $NO_x$ are high oxygen availability and high cylinder temperature which is just opposite to that of the causes of emissions of CO and HC. The emission of $NO_x$ with respect to the brake power for the coated and uncoated engines is shown in fig. 6. The $NO_x$ emission was found to be varied linearly with the load. The $NO_x$ emission unlike the emission of CO and HC was found to be increased in the coated engine than the uncoated engine. It was found that the $NO_x$ emission of the coated engine was 24.4% higher than that of the coated engine for diesel and 7.7% for SME B100. The main reason for this increased emission of $NO_x$ is increased combustion duration in the coated engine which enables the oxidation of nitrogen into $NO_x$. This is the major disadvantage of the coated engine. In order to eliminate this problem, CNT was injected into the diesel. By adding CNT, 21.15% decrease of $NO_x$ was found in the low heat rejection engine fueled with SME B100.

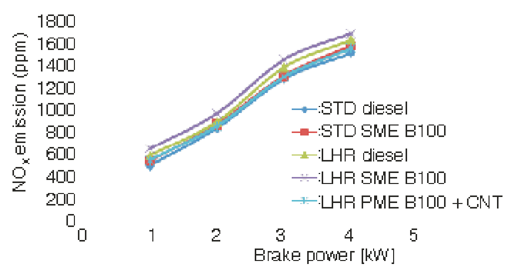

**Figure 6. Emission comparison of $NO_x$**

## Conclusion

The enhancement in brake thermal efficiency of the coated engine is observed compared to uncoated engine. The reduction in specific fuel consumption and emission of CO, HC is observed for the coated engine compared to the uncoated engine. The emission of $NO_x$ is found to be higher for the coated engine, whereas the reduction in values is observed for CNT added biodiesel. Therefore, the $LaAlO_3$ coated engine operated with CNT mixed SME is found to be the best combination among the five combinations in which the analysis was carried out.

## Acronyms

CNT – carbon nanotubes
KOH – potassium hydroxide
PSZ – partially stabilized zirconia
STD – standard
SME B100 – 100% sunflower methyl ester and 0% diesel
YSZ – yttrium stabilized zirconia

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Paper submitted: September 6, 2015
Paper revised: January 3, 2016
Paper accepted: February 9, 2016