Effect of lanthanum zirconate thermal barrier coating on the performance and emissions of a diesel engine using biodiesel

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Abstract. An experimental Lanthanum Zirconate (La₂Zr₂O₇) ceramic powder has been used as a thermal barrier coating material to study its effect on performance and exhaust emissions of a single cylinder diesel engine operated using diesel and biodiesel. Pongamia vegetable oil has been used to prepare biodiesel through transesterification process. Lanthanum doped thermal barrier coatings are found to be promising candidates for applications such as in diesel engines besides the conventional YSZ TBCs with lower thermal conductivity, high sintering resistance, low oxygen permeability and with catalytic activity. This experimental study has shown that the performance of the engine is improved significantly on the account of brake thermal efficiency and specific fuel consumption. Emissions, on the other hand are also improved, especially the smoke opacity which is significantly low at all Low Heat Rejection (LHR) operations.

1. Introduction

Internal combustion engines, whose components that are exposed to combustion are coated with a thermal barrier coating, are often called as low heat rejection (LHR) engines [1]. The objective of this concept is to reduce the fuel consumption by eliminating the generally used cooling system of the engine and convert a part of excess energy available in the exhaust in to useful work. Plasma-sprayed ceramic thermal barrier coatings (TBCs) have been the extensively perused area of interest from the recent past for the improved efficiency and reduced emissions especially in diesel engines. 8% Yttria stabilized zirconia, also called partially stabilized zirconia(Y-PSZ) material has been a reliable TBC for high temperature applications. However, investigations are going on to develop more reliable TBC materials prompted by the failure of PSZ coating at higher temperatures with continuous thermal loads as in diesel engines. The main parameters that are limiting the usability of PSZ coating by a catastrophic delamination are phase transitions and increased sintering above 1200°C. Also, high Oxygen permeation through pores causes oxidation of bond coat resulting in coating failure [2,3,5].

There are a significant number of research articles presented over the years on the effect of different thermal barrier coatings on the diesel engine using different fuels. It has been observed from most of the literature that the application of TBCs on the engine parts resulted in improved engine performance with decreased emissions, especially emissions like CO, HC and smoke opacity [6-10].

In diesel engines, usage of biodiesel and its blends is restricted to a certain limit because of their lower heating values which increases the fuel consumption to develop the same amount of power though the tailpipe emissions are less. This increased fuel consumption should be met with higher

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production rates of biodiesel and its blends in order to make the biodiesel a sustainable fuel. A lot of research is being done to increase the efficiency of diesel engines when run using biofuels using different techniques [9]. Among them is the application of thermal barrier coatings, because of which heat loss to different engine components is restricted to a certain limit and making use of the resultant in-cylinder temperatures to gain maximum energy out of biodiesel fuels.

The major drawback for the usage of vegetable oils in diesel engines is high viscosity and low volatility [4]. Esterification of vegetable oil to its methyl ester reduces its molecular weight and viscosity and increases its Cetane number. The insulation of the combustion chamber with TBC influences the combustion processes and hence the performance and emissions of the engine [8].

To obtain better combustion characteristics in a diesel engine using biodiesel fuels, given the proven outcome of TBCs in diesel engines, a novel and competent candidate material need to be developed. While there are many such materials under development, Lanthanum Zirconate (La₂Zr₂O₇) has gained importance due to its superior thermomechanical properties such as high sintering resistance and phase stability at elevated temperatures with lower thermal conductivity [3,4,19].

As the vegetable oils need higher chamber temperatures to achieve efficient energy release rates, the concept of low heat rejection has been attempted in the present study. The proposed concept consists of an insulated engine whose piston, valves and cylinder head are coated with Lanthanum Zirconate thermal barrier coating material and the experiments were carried with a biodiesel prepared from Pongamia oil.

2. Experimental setup and Procedure

Table. 1 shows the specifications of the test engine employed in the study The fuels used are standard diesel, B100 or pure biodiesel prepared from Pongamia Pinata vegetable oil through transesterification process. The measured fuel properties are given in Table.2. Fuel flow rate was measured with the help of a calibrated burette. Air flow rate into the engine is measured using an air box and an U-Tube manometer. A multi gas analyser made (Netel, model NPM-MGA-2) was used to measure the exhaust gas emissions. Particulate emissions are measured using a smoke meter (Netel, model no.NPM-SM-111B). Lanthanum zirconate coated engine components, piston, cylinder head and valves have been shown in Fig.1 and the schematic diagram of the experimental setup has been shown in Fig.2.

A separate fuel filter has been used for each fuel to prevent the deterioration of results because of the difference in viscosities and densities of different fuels. Thermocouples are arranged at different locations to measure the temperatures at different locations viz. engine coolant outlet temperature, exhaust gas temperatures etc. Biodiesel has been prepared from Pongamia vegetable oil using transesterification process. Methanol has been used as alcohol and Sodium Hydroxide (NaOH) of 3 percent (wt/vol) has been used as a catalyst in the transesterification process. A molar ratio of 1:6 (oil to methanol) has been used to ensure the completion of the reaction. A magnetic stirrer with heating facility has been used to maintain 60° C, at an RPM of 700 for proper mixing and the reaction time is set to 2 hours. A yield of 92 percent has been obtained from the process.

Experimental lanthanum zirconate (La₂Zr₂O₇, LZ) powder, that was prepared using solid state reaction method was procured from Star Earth Minerals Private Limited, Mumbai with a grain size of 55 microns as recommended for the plasma spray coating. Spray coatings were done on the engine components at Sri Sai Surface coating Technologies, Hyderabad using the plasma spray system type MP 200 from AMT AG, Switzerland. The process parameters used were taken from the literature and are presented in Table.3 [3]. 500 microns material was machined off the engine components prior to the application of TBC coating. This to maintain the compression ratio of the engine constant even after applying the TBC coating. 350 microns bond coat (NiCrAlY) was applied on the engine components and then the LZ coatings was applied with a thickness of 150 microns. The thickness of the coating is measured using Minitest650 from Elektrophysik.

Experiments were conducted initially on the standard engine i.e. without any coating applied to the engine parts using standard diesel and B100. La₂Zr₂O₇ TBC coated engine parts are then assembled to the engine and experiments were conducted similarly as mentioned above for the standard engine. All
the experiments were conducted at standard injection timing of 23° BTDC and at 200 kg/cm² injector opening pressure as specified by the manufacturer.

Table 1 Specifications of the test engine

| Parameter               | Value |
|-------------------------|-------|
| No. of cylinders        | One   |
| Bore, mm                | 80    |
| Stroke, mm              | 110   |
| Cubic capacity, CC      | 553   |
| Rated output, kW (HP)   | 3.68 (5) |
| Compression Ratio       | 17:1  |
| Type of Injection       | Direct |
| Injection Timing, ° BTDC| 23    |
| Injector Opening Pressure, kg/cm² | 200 |
| Type of cooling         | water |
| Rated speed, RPM        | 1500  |

Table 2 Fuel properties of standard diesel and B100

| Property                        | Diesel | B100 |
|---------------------------------|--------|------|
| Density @30°C                   | 832    | 891  |
| Viscosity @30°C, Cst            | 2.2    | 4.08 |
| Calorific Value, kJ/kg          | 43626  | 38540|
| Flash Point, °C                 | 35     | 174  |
| Cetane Number                   | 48     | 56   |

Table 3 Plasma spraying parameters [3]

| Parameter                              | Value |
|----------------------------------------|-------|
| Arc Current Intensity (A)              | 660   |
| Primary gas (Ar) flow rate, slpm       | 30    |
| Secondary gas (H₂) flow rate, slpm     | 16    |
| Spray distance, mm                     | 130   |
| Carrier gas flow rate, slpm            | 4     |

Fig. 1 La₂Zr₂O₇ coated engine components

Fig. 2 Schematic diagram of the experimental setup

3. Results and Discussions

The results obtained from the experiments conducted on the standard and coated engine are presented below. The standard tests are mentioned as std for all fuels and the Lanthanum Zirconate coated test results are mentioned as LZ and are referenced with standard engine results. Fig 3 shows the variation of brake specific fuel consumption (BSFC) with respect to brake power obtained with standard as well as LZ coated Low Heat Rejection (LHR) engine using different fuels. As it can be seen from the figure, the LZ coated engine has a BSFC which is significantly low compared to that of standard engine operation with both diesel and biodiesel. The increased engine temperatures in the cylinder because of the insulation are believed to have helped in releasing maximum energy from combustion with reduced heat transfer to the engine components. The LZ
coated engine is found to have 11.1% lower BSFC with diesel compared to that of standard diesel operation and 11.8% lower at full load when run using B100 compared to that of standard operations with B100 fuel. It can be observed that B100 when run with an LZ coated engine has resulted in decreased specific fuel consumption compared to standard B100 operation. This resulted in consuming less fuel for the development of the same amount of power. The BSFC trends observed are in well agreement with most of the literature found on thermal barrier coatings [18,21].

Fig.4 shows the variation of brake thermal efficiency with brake power for the standard and an LZ coated LHR engine using different fuels. LZ LHR engine when run with standard diesel has shown 11% improvement in the brake thermal efficiency compared to the standard diesel operation and the improvements when run with B100 are observed to be 12% to that of standard B100 operation at full load. The lower heating value and higher density of biodiesel, which resulted in higher fuel consumption and lower thermal efficiency of standard engine operation are compensated when run with the LHR engine operation. It is assumed that the higher cylinder temperatures, specifically in the case of biodiesel LHR operation helped in improved combustion along with the characteristic advantage of biodiesel carrying molecular oxygen with it resulting in the maximum release of its energy.
Fig. 5 shows the variation of CO emissions with brake power at standard and LHR engine operation of the engine. Carbon monoxide is formed during combustion of fuel-rich mixtures due to deficiency of oxygen. As CO emissions depend mainly on mixture quality, in-cylinder temperature and pressures, the higher cylinder temperatures favor the oxidation of CO emissions and result in low values even at low engine loads. The LZ LHR engine run with diesel has emitted above 18% low CO emissions compared to that of standard diesel operation. When run using LHR B100 CO emissions are 15% less than that of standard B100 engine operation at full load. The oxygen molecules present in the B100 might also have helped the better combustion of the fuel and therefore resulted in lower CO emissions in all LHR engine operations compared to that of standard engine tests.

Fig. 6 shows the variation of unburnt hydrocarbon emissions from the test engine using different fuels at standard and LHR engine operating conditions. Unburnt hydrocarbons are those which escape the cylinder without participating in the combustion process. It has been observed from the experimental results of HC emissions that the TBC applied helped in better mixing of fuel particles with the available air rapidly in the cylinder resulting in low HC emissions. It is also assumed that the catalytic nature of the LZ may have played a dominant role in oxidizing unburnt hydrocarbons within the cylinder. A reduction of 29% HC emissions with LHR diesel operation compared to standard diesel operation and a reduction of 23% with LHR B100 compared to standard B100 operations at full load has been observed in the investigation. The HC emissions can further be reduced if the injection parameters are adjusted and tuned to make maximum advantage of the insulation.

Fig. 7 shows the variation of NO\textsubscript{x} emissions with brake power with and without coating using different fuels. The biofuels have resulted in higher NO\textsubscript{x} emissions even at standard engine operation. This is an expected outcome since the biodiesel carry around 10% molecular oxygen with it. This molecular oxygen helps in improving combustion, therefore resulting in higher heat release rates which are major contributors to the formation of NO\textsubscript{x}. The NO\textsubscript{x} emissions released when B100 is used as fuel is significantly higher; this is attributed to the advanced injection of biodiesel because of its low compressibility than the standard diesel. NO\textsubscript{x} emissions are found to be high in all operations of LHR engine using different fuels because most of the NO\textsubscript{x} formed in IC engines are thermal NO\textsubscript{x} and are temperature dependent. NO\textsubscript{x} from LHR engine operations found to be 17% and 9% higher using diesel and B100 compared to that of standard diesel and B100 operations at full load. The higher NO\textsubscript{x} emissions from the LHR engine are in good agreement with the findings of other researches [4,11,22].

Fig. 8 shows the variation of smoke opacity with brake power at different engine operations. Smoke emissions from diesel engines are majorly soot which is a carbonaceous particulate matter and is produced during combustion of the rich fuel - air mixtures. The net soot emissions depend upon the rates at which soot particles are produced and oxidized. Temperature plays an important role in net
soot emissions. Temperature on one hand increases soot oxidation while on the other hand increases fragmentation of fuel molecules that may lead to higher soot formation. The effects of several interacting factors thus govern the net soot emissions. It has been observed in the present investigation that the LZ LHR engine developed low smoke with all the fuels compared to that of standard engine tests. LHR engine using diesel fuel emitted 18% less smoke emission compared to the standard engine. The LHR B100 soot emissions were 15% lower at full load compared to the non-coated engine operation. Most of the soot developed gets consumed or oxidized within the cylinder because of the higher in-cylinder temperatures. Similar observations were noticed in other studies that reported reduced smoke emissions [23, 24].

4. Conclusions
In the present investigation, an experimental TBC has been made using Lanthanum Zirconate as candidate material and a series of experiments have been conducted on a single cylinder direct injection diesel engine using diesel and biodiesel as fuels. Biodiesel has been prepared from pongamia oil through transesterification process. Following conclusions are made based on the experimental results:

1. Experimental observations showed that the LZ has a positive effect in improving engine performance with reduced emissions with both the test fuels.

2. The BSFC has been found to be 11.1% and 11.8 % lower with LZ diesel and B100 operation compared to that of standard engine operations using same fuels.

3. Brake thermal efficiency of the LHR engine B100 is improved significantly compared to that of standard engine operation resulting in 12% improvement.

4. CO emissions are reduced with LHR operation significantly. Higher CO emissions from standard engine using diesel fuel are attributed to the non-favorable conditions for the oxidation of CO into CO$_2$ especially at no load and full load conditions. This problem has been overcome using TBCs which helped to oxidize the CO emissions formed within the cylinder.

5. TBC operation of the test engine resulted in increased NO$_x$ emissions. Standard engine operation with B100 has produced higher NO$_x$ than the standard diesel fuel. The insulation has resulted in 17% and 9% higher NO$_x$ using diesel and B100 fuels.

6. A reduction of 29% and 23% in hydrocarbon emissions has been observed with LHR engine operation using diesel and B100 fuels respectively. The higher cylinder temperatures are believed to have helped in reducing the HC emissions by complete mixing of fuel vapor with available air for the improved combustion.

7. Smoke emissions are significantly low using B100 fuel compared to standard diesel fuel. The smoke emissions are 18% and 15% low with LZ LHR engine operation compared to that of standard engine operations using diesel and B100 fuels. The characteristic nature of LZ catalytic activity may have helped to oxidize the soot formed in the cylinder and resulting in low smoke emissions.

It can be concluded based on the experiments that the lanthanum zirconate (LZ) TBC has a higher potential to replace the existing TBC materials with improved engine performance and reduced emissions.

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