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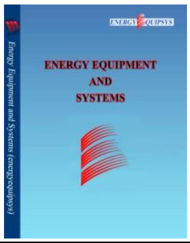

The effect of a novel hybrid nano-catalyst in diesel-biodiesel fuel blends on the energy balance of a diesel engine

Authors

Behdad Shadidi [a]
Hossein Haji Agha Alizade [a*]
Barat Ghobadian [b]

[a] Department of Biosystems Engineering, Faculty of Agriculture, Bu-Ali Sina University, Hamedan, Iran

[b] Department of Biosystems Engineering, Faculty of Agriculture, Tarbiat Modaress University, Tehran, Iran

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ABSTRACT

In internal combustion engines, only about a third of the total fuel input energy is converted into useful work. If the energy rejected into the cooling system and the exhaust gases could be recovered instead and put into useful work, fuel economy would have been substantially improved. The main aim of this research paper was to evaluate the effects of the hybrid nano-catalyst containing cerium oxide and molybdenum oxide in amide-functionalized multiwall carbon nano-tubes (MWCNTs) on the thermal balance of a diesel engine using two types of diesel-biodiesel blends (B5 and B10) in three concentrations (30, 60, and 90 ppm). The research engine was a single-cylinder, four-stroke, direct-injection, and air-cooled diesel engine. The engine was run at two speeds (1,700 rpm and 2,500 rpm) in full load conditions. The thermal efficiency (useful work) resulting from the energy transferred into the cooling system, the exhaust gases, and the unaccounted losses, including the lubricating oil heat loss and the convection and radiation heat transfer, were computed using the first law of thermodynamics. The results showed that by increasing the amount of nano-catalysts (cerium oxide and molybdenum oxide) in fuel blends, the energy transferred to the cooling system and exhaust gases were decreased. The highest reduction in the energy transferred to the cooling system and the exhaust gases was 5.38% and 2.26% for B5, containing 90 ppm ($B5_{90ppm}$), and 5.61% and 2.62% for B10, containing 90 ppm ($B10_{90ppm}$) respectively. Also, the thermal efficiency went up. Compared with the nano-catalyst-free fuel blends, the highest increase in thermal balance was observed as 6.75% and 5.41% for $B5_{90ppm}$ and $B10_{90ppm}$ respectively.

Keywords: Energy Balance, Nano-Cerium Oxide, Nano-Molybdenum Oxide, Diesel Engine, Biodiesel.

1. Introduction

The main sources of energy in the world are petroleum, gas, and coal. All three are non-renewable. Due to an increase in petrol prices and also environmental considerations, researchers are now trying to find renewable energy sources that could replace fossil fuels [27]. They have proposed several solutions. One is to improve both the mentioned concerns simultaneously by using biodiesel fuel [18]. Biodiesel is non-toxic and environment-friendly and can be used either in its pure form or blended with diesel fuel in any proportion, without any further modifications [1]. Using biodiesel as a fuel reduces engine power and increases fuel consumption and NOx emission [31].

*Corresponding author: Hossein Haji Agha Alizade
Address: Department of Biosystems Engineering, Faculty of Agriculture, Bu-Ali Sina University, Hamedan, Iran
E-mail address: h-alizade@basu.ac.ir

Heterogeneous or homogeneous catalysts can be used to improve the performance of biodiesel-fed engines and decrease emission as much as possible [19].

The use of nano-science to develop the production of renewable and sustainable energy is one of the most important challenges of the 21st century. Nano-catalysis is a new field in catalyst science that has attracted everyone's attention [4].

Smaller particles have greater catalytic activity because of their large surface area per unit volume [23–25]. Also, nano-scale particles spread more uniformly within the liquid fuel and are more stable than those out of this range. So, nano-catalysts are much more effective [16–29].

Therefore, numerous studies have been conducted on the influence of nano-particles as an additive to various fuel blends in IC engines to improve diesel and biodiesel combustion.

Banapurmat and his colleagues performed experimental investigations on a single-cylinder four-stroke diesel engine fuelled with biodiesel and multi-walled carbon nano-tubes (MWCNT) blends to determine engine performance, combustion, and emission characteristics. They used the catalyst at two different ranges of 25 ppm and 50 ppm. They reported considerable enhancement in the brake thermal efficiency with reduced exhaust pollutants from the engine due to the addition of nano-particles to biodiesel fuel [7].

Selvan and the other researchers used cerium oxide nano-particles (CERIA) and carbon nano-tubes (CNT) (each 25, 50, 100 ppm) as additives in the diesterol (diesel-biodiesel-ethanol) blends to establish the performance, combustion, and emission characteristics of a variable compression ratio engine. They found that brake thermal efficiency increases up to 7.5% with the addition of cerium oxide and CNT in diestrol blends. They also found a remarkable decrease in harmful exhaust emissions of the variable compression ratio engine [5].

Vairamuthu and others carried out an investigation on the performance and emission characteristics of biodiesel with and without CERIA in the DI diesel engine. They showed that the use of CERIA as an additive in the B100+20 ppm CERIA blend reduced harmful exhaust pollutants. The brake thermal efficiency was observed to be 25.09%. It was 21.61% for the B100 in full-load engine conditions [30].

In another study, Mirzajanzadeh and his colleagues applied the hybrid nano-catalyst containing CERIA on amide-functionalized MWCNT into two diesel-biodiesel blends (B5 and B20) in three concentrations (30, 60 and 90 ppm) to enhance the performance of heavy-duty DI diesel engines. The results revealed that power and torque increased by up to 7.81% and 4.91% respectively and fuel consumption decreased by 4.50% [19].

Increasing the efficiency of an internal combustion engine is another solution that has got focus recently [28]. The input energy in the internal combustion engine is divided into four parts: (1) brake power (useful work), (2) energy transferred to coolant or cooling heat loss, (3) energy lost to exhaust or exhaust heat loss, and (4) unaccounted heat loss or the miscellaneous heat loss that covers mainly the convection and radiation heat losses. Also, some researchers consider the lubricating oil loss as unaccounted heat loss [2, 9, 11, 20, 33].

The energy balance of IC engines is an analysis of the first law of thermodynamics. It is also called the heat balance or thermal balance [2].

The second law stipulates that it is impossible to obtain 100% efficiency. In other words, all the input energy cannot be converted into useful work [28].

In another investigation, decreasing heat losses from an engine cylinder caused a small increase in brake horsepower. About a third of the input energy was converted to useful work (brake work). Much attention has been given to increasing the brake horsepower of an internal combustion engine by reducing the energy loss during the engine cycle [9].

Abedin and his co-workers applied palm and jatropha biodiesel blends to evaluate performance, emissions, and heat losses in a diesel engine. They used B5, B10, and B20 of palm and B10 and B20 jatropha biodiesel for the speed range of 1000 to 4000 rpm at full load and compared the effects with those of diesel fuel. The results indicated that with the increasing biodiesel percentage in the blends at all speeds, both the lubricating oil heat loss (Qoil) and the water heat loss (Qw) increased by 6% to 9.5% and 0.8% to 4.7% for using 10% and 20% blends respectively. The exhaust heat loss decreased by 1.5% to 8.0% for an addition of 10% biodiesel [1].

Khoobbakht and colleagues analysed the energy and exergy and investigated the effects of the levels of biodiesel-ethanol-diesel fuel blends on a DI diesel engine. In the case of energy analysis, they reported mean work output and total energy loss rates of 41.22 kW and 71.36 kW respectively. Around 63% of the input energy was lost in various ways from the control volume, and only 37% of the input energy was converted into mechanical energy [14].

In a different study, Ramadhas and his co-workers theoretically and experimentally evaluated the energy balance of a diesel engine operating on rubber seed oil methyl ester, diesel fuel and their blends. Their findings revealed that the brake thermal efficiency of biodiesel was lower than that of the diesel fuel. The peak pressure was lower and the peak temperature was higher while using rubber seed oil. Finally, the heat loss from the diesel-fuelled engine was lower than the biodiesel-fuelled engine [21].

Canakci and Hosoz tried to determine the energy balance of diesel engines operating on soybean oil methyl ester (SME), yellow grease methyl ester (YGME), and No.2 diesel fuel in a 20% fuel blend. The results indicated that the brake thermal efficiency for SME, YGME, and their blends was slightly higher than that for No.2 diesel fuel. When the engine was operated on SME and YGME, all the heat losses together, ignoring exhaust loss, were 4% and 3.1% higher than that for No.2 diesel fuel respectively. The exhaust loss of the biodiesels in this experiment was lower than that of No.2 diesel fuel [8].

As far as the present study is concerned, the nano-cerium oxide and molybdenum oxide were hybridized with carbon nano-tube multiwall (CNTMW) as a nano-additive. It was added to diesel-biodiesel fuel blends, B5 (95% diesel and 95% biodiesel) and B10 (90% diesel and 10% biodiesel) at full engine load, two different engine speeds (1,700 rpm, 2,500 rpm) and three concentrations (30ppm, 60ppm, 90ppm). For each blend, an equal amount of cerium oxide and molybdenum oxide was used. For example, 30 ppm of nano-catalyst has 15 ppm of cerium oxide and 15 ppm of molybdenum oxide. Finally, the thermal balance of the diesel engine under test was fuelled by a diesel-biodiesel nano-catalyst, and the variation of output power, the energy transferred to the cooling system, and the exhaust gas energy were investigated and compared experimentally.

Nomenclature

B5	Biodiesel 5% + Diesel 95%
B10	Biodiesel 10% + Diesel 90%
$B5_{90ppm}$	B5 + 90 ppm nano-catalyst
$B10_{ppm}$	B10 + 90 ppm nano-catalyst
Ce	Cerium
C	Specific heat (kJ/kgK)
$\dot{m}$	Mass flow rate (kg/s)
P	Power (kW)
Q	Heat (kJ)
N	Engine speed (rev/s)
Mo	Molybdenum
DI	Direct Injection
IC	Internal Combustion
MWCNT	Multiwall Carbon Nano-Tube
CO_2	Carbon dioxide
T	Temperature (K)
CNT	Carbon Nano-Tube
CO	Carbon monoxide
HC	Hydrocarbons
NO_x	Nitrogen oxides

Subscripts

s	supplied
cool	Coolant
un	unaccounted
LHV	Lower Heat Value
g	Gas
b	brake
exh	exhaust
f	fuel
a	air
e	exhaust gas

2- Material and Methods

2-1 Fuel and Nano-catalysts' preparation

The transesterification reaction of catalyzed KoH (oil/methanol ratio: 7/1. 1 wt% KoH) was used to produce biodiesel from waste cooking oil. The diesel-biodiesel fuel blends were prepared based on volume percentage (B5, B10). The letter 'B' stands for 'biodiesel' and each number represents the volume percentage of each biodiesel fuel. For example, B5 means the blend contains 5% biodiesel and 95% diesel fuel.

Some important characteristics of fuel blends were measured. Table 1 shows the instruments that were used to determine the fuel blend properties.

Nano-cerium-oxide-molybdenum-oxide was hybridized with MWCNTs (5%) using the integration method. It was then calcinated at 400ºC for three hours. The hybridized product was carboxyl-functionalized, first by ozonation at room temperature and in atmospheric condition for four hours. One gram of ozonized powder was dispersed in 500ml Toluene. Then, 1 gram Acetyl Amin was added. The solution was autoclaved for 24 hours and then refluxed in a 1000 ml balloon for six hours. To remove the excess amine after cooling it at room temperature, the amidated product was isolated by a simple filtration method. It was then washed with tetrahydrofuran and 50ml and 100ml distilled water respectively. The final product, containing Ce, Mo, and amides functional group, was dried at 90°C for an hour.

Finally, after preparing the nano-catalyst, it was added to B5 and B10 fuel blends in three concentrations (30, 60, and 90 ppm) and sonicated in an ultrasonic bath for 20 minutes (40 HZ) to achieve better dispersing and highly stable fuel blends.

2-2 Thermal balance calculation

The internal combustion engine can be considered as a thermodynamic open system. It is a useful concept for understanding the thermodynamic behaviour of the system. It is related to the idea of control volume—a space enclosing the system and surrounded by an imaginary surface, which is often called the 'control surface' (Fig. 1). It is possible to visualize the inside of the system by drawing up an energy balance sheet of the inflows and outflows, if one can recognize all the mass and energy flows into and out of a system [2-11].

If a control volume around the engine is considered to calculate the energy balance in the engine, then the steady flow according to the first law of thermodynamics for this control volume is as follows [11-13]:

$$Q_s = P_b + Q_{cool} + Q_{exh} + Q_{un} \quad (1)$$

where Q_s is the energy supplied by the fuel. It is explained by

$$Q_s = \dot{m}_f \times Q_{LHV} \quad (2)$$

where Q_{LHV} and $\dot{m}_f$ are the lower calorific

Table1. List of the main test instruments for determining fuel properties

	Characteristics	Equipment	Type
1	Density	Digital density meter	VIP-2MP model, Russia
2	Viscosity	Stabinger viscometer	SVM-3000 model, Anton Paar Co, Austria
3	Cloud point and pour point	Refrigerator Art	500/s model, Italy
4	Flash point	Grabner FLPH mini flash point tester	Grabner, Austria

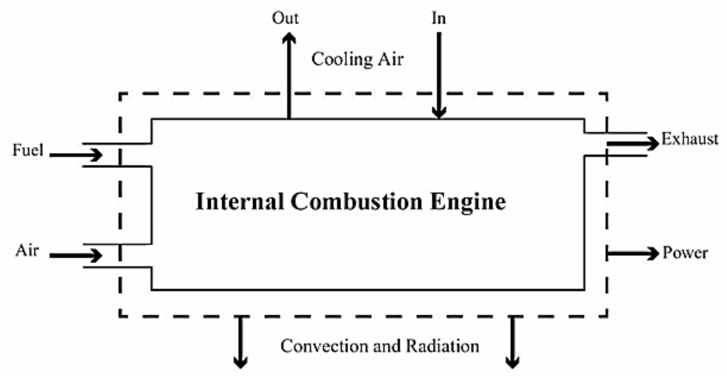

Fig.1. Control volume of the internal combustion engine

value and the mass flow rate of the fuel respectively, and P_b is the brake power, which can be calculated by

$$P_b = \frac{2 \times \pi \times N\left(\frac{rev}{s}\right) \times T(N.m)}{10^3} \quad (3)$$

where T and N are the engine torque and speed respectively.

Q_{cool} is the rate of heat transfer to the cooling system, which can be computed by using the following equation:

$$Q_{cool} = \dot{m}_a \times C_a \times \nabla T_a \quad (4)$$

where $\dot{m}_a$ and C_a are the mass flow rate and specific heat of the air respectively and ∇T_a is the temperature difference between the inlet and outlet cooling air.

Q_{exh} is the exhaust heat loss. It is calculated by considering the heat necessary to increase the temperature of the total mass (fuel + air) from the outside conditions (T_a) to the temperature of the exhaust (T_g). It is necessary to calculate the mean specific heat of the exhaust gases (C_e), which, in this case, is assumed to be the specific heat of air at the mean exhaust gas temperature [15–20].

The equation for exhaust heat loss calculation is:

$$Q_{exh} = (\dot{m}_f + \dot{m}_a) \times C_e \times (T_g - T_a) \quad (5)$$

Finally, Q_{un} is the unaccounted heat loss, that is, the heat rejected into the oil (if separately) plus radiation and convection from the engine's external surface.

The unaccounted heat loss can be estimated by applying the subtraction rule [3–28]:

$$Q_{un} = Q_s - (P_b + Q_{cool} + Q_{exh}) \quad (6)$$

2-3 Engine test setup

The experimental set-up consists of a four-stroke, air-cooled, single-cylinder diesel engine. The general details of the engine specifications are given in Table 2 and the schematic diagram of the experimental setup is illustrated in Fig. 2.

The engine brake power was measured by a WE400-Mobtakeran-ParsAndish eddy-current dynamometer. A K-type thermocouple and an air-flow meter were used to measure the temperatures in different locations and air consumption respectively. All the measurement data were recorded and collected by a digital data-acquisition system. The engine was run at two speeds (1,700 rpm and 2,500 rpm) in full load conditions to evaluate the energy balance of the diesel engine running on diesel-biodiesel-nano-catalyst blends. Each test was repeated thrice to ensure the reliability of the data.

3.Results and discussion

3.1.Fuel properties

Some important physicochemical properties of the produced biodiesel were measured. These have been summarized in Table 3.

3.2.Engine Brake Power (P_b)

The final output power of the engine is known as the brake power, which is the useful power delivered by an engine. It is also called the brake thermal efficiency when it is expressed according to the percentage of input energy.

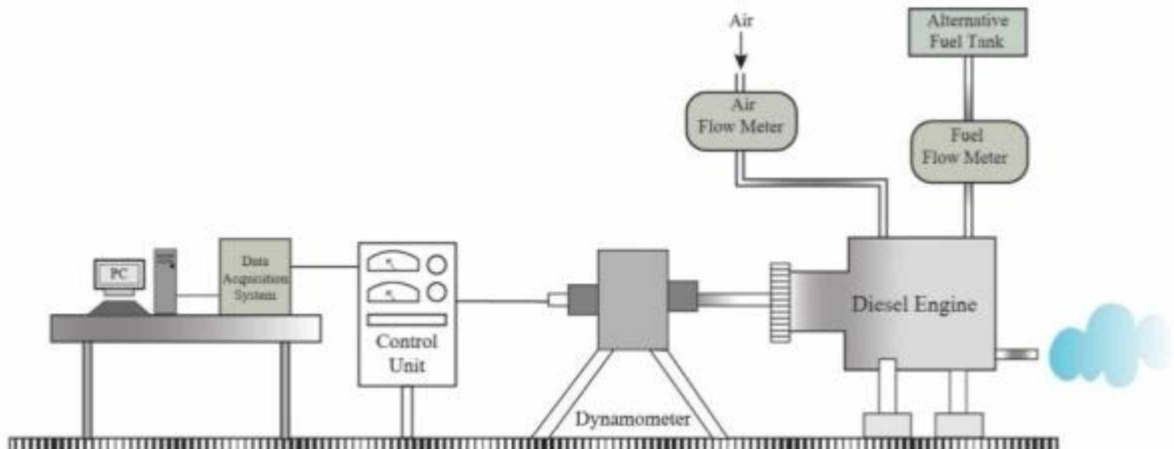

Fig.2. The schematic diagram of experimental setup

Table 2. Engine Specifications

Type	**Lombardini 3LD 510**
Number of cylinders	1
Bore	85 mm
Storke	90 mm
Volume	510 Cm^3
Compression ratio	18,1:1
Maximum power at 3000 rpm	9 kW
Maximum torque at 1800 rpm	33 N.m

Table 3. Physicochemical properties of the produced biodiesel

Property	**Produced Biodiesel**	**Limits according to ASTM D6751**	**Units**
Density(@15°C)	0.8767	0.82–0.9 according to EN ISO 12185	g/ml
Viscosity(@40°C)	4.85	1.9–6 according to ASTM D 445	mm^2/s
Flash Point	176	>93 according to ASTM D93	°C
Pour Point	5	According to ASTM D 874	°C
Cloud Point	11	according to ASTM D 874	°C
Water and sediment	0.05	<0.05 according to ASTM D 2709	%volume
Cetane number	97.2	>47 according to ASTM D 613	----

Figures 3 and 4 illustrate the thermal efficiency of B5 and B10 fuel blends in full load with three concentrations of nano-catalyst at engine speeds of 1,700 rpm and 2,500 rpm respectively.

Figures 3 and 4 show that compared with their nano-catalyst-free counterparts, thermal efficiency increases with an increase in the amount of the nano-catalyst in the fuel blends in both engine speeds. The addition of the nano-catalyst at 30, 60, and 90 ppm is responsible for an increase in thermal efficiency by 0.5%, 2.36%, and 5.41% for B5, and 2.33%, 4.96%, and 6.75% for B10 at 1,700 rpm, and by 1.11%, 2.39%, and 3.47% for B5, and 2.11%, 3.7% and 4.8% for B10 at 2,500 rpm respectively.

Fuel reacts with oxygen to release energy at its ignition temperature point. A plentiful supply of oxygen causes a complete combustion. On the other hand, when oxygen supply is insufficient, incomplete combustion occurs. The synthesized nano-catalyst in this research, containing nano-cerium oxide and nano-molybdenum oxide, supplies oxygen molecules in a chain reaction. This leads to improved combustion. Also, synthesized nano-catalyst, as an additive to fuel blends, provides millions of nano-clusters caused by their explosion. The sediments and deposits are disintegrated and their reformation is prevented. Hence, cerium oxide and molybdenum oxide prevent the formation of iron and carbon deposits, which leads to decreased friction in the mentioned moving part of the engine [22–29]. These two reasons lead to an increase in engine power and, subsequently, an increase in the thermal efficiency of the engine. The thermal efficiency of the B5 was slightly higher than that of B10. This could be attributed to the lower heating value of the biodiesel which is responsible for this reduction [1, 10, 13, 32].

3-3 Energy transferred to cooling system

The energy transferred into the cooling system decreased with an increase in nano-catalyst concentration in the blends at both engine speeds (Figs. 5 and 6).

It can be seen from Fig. 5 that compared with its nano-catalyst-free counterpart, the nano-catalyst at 30, 60, and 90 ppm leads to 2.65 %, 4.58%, and 5.38% decrease in air head loss at 1,700 rpm, and 1%, 1.3%, and 2.33% decrease in the energy transferred into the cooling system at 2,500 rpm respectively.

Figure 6 shows that compared with the B10 nano-catalyst-free version, the air-heat loss reduction was 3.28%, 4.74%, and 5.61% at 1,700 rpm and 1.27%, 2.04%, and 2.81% at 2,500 rpm respectively.

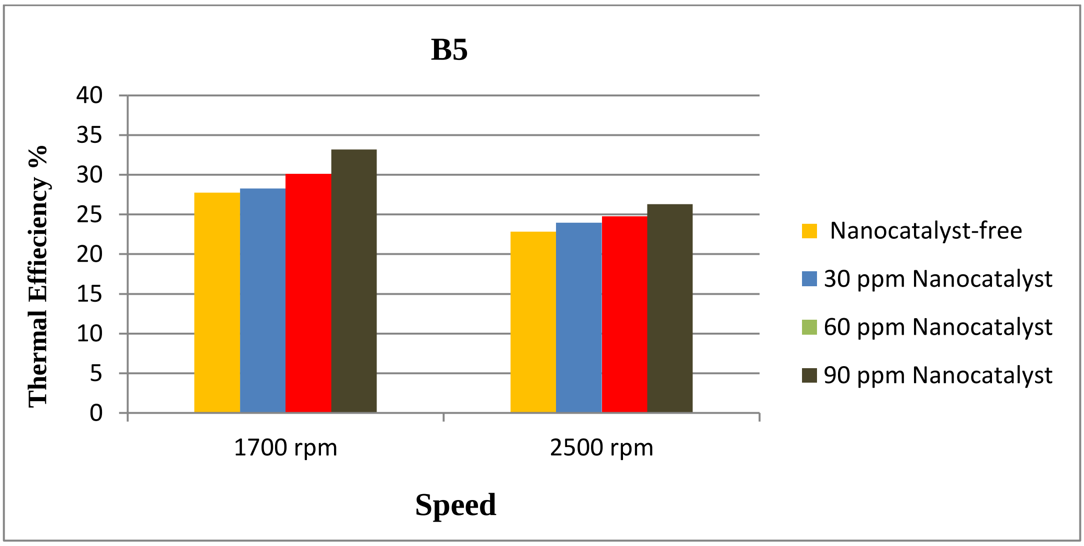

Fig.3. Thermal efficiency analysis for different nano-catalyst concentrations and B5 fuel blend

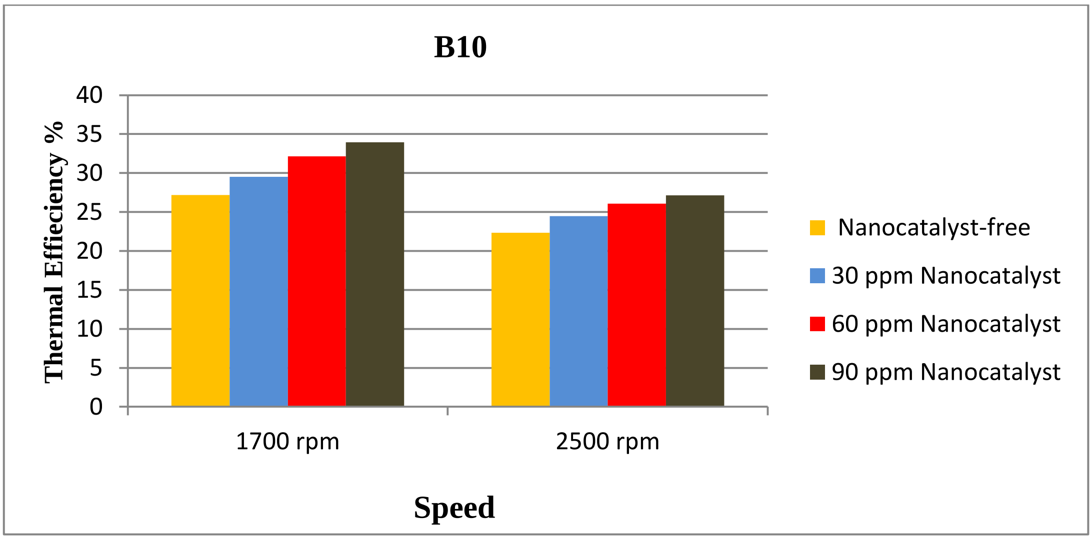

Fig.4. Thermal efficiency analysis for different nano-catalyst concentrations and B10 fuel blend

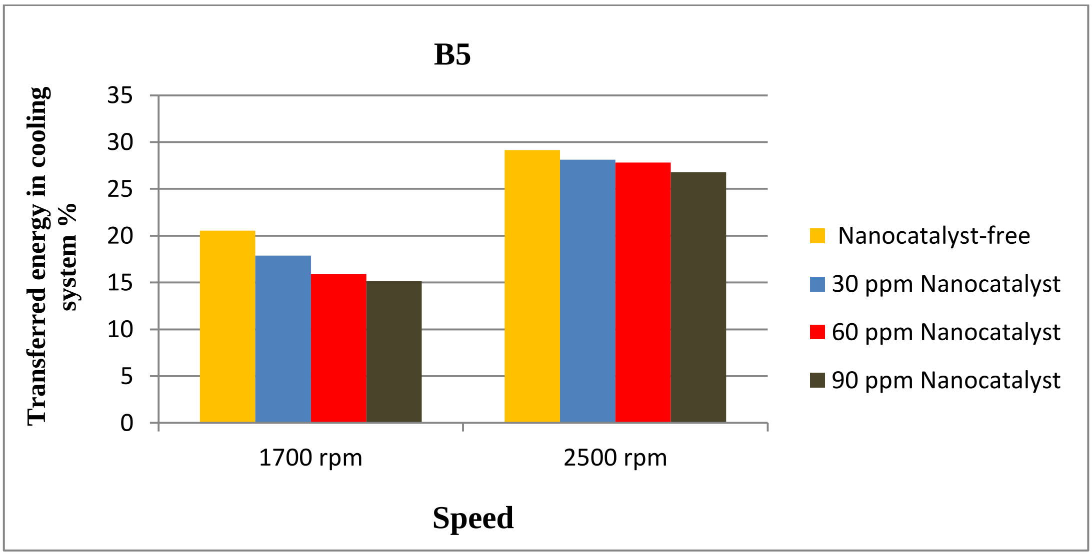

Fig.5. Analysis of the energy transferred into the cooling system for different nano-catalyst concentrations and B5 fuel blend

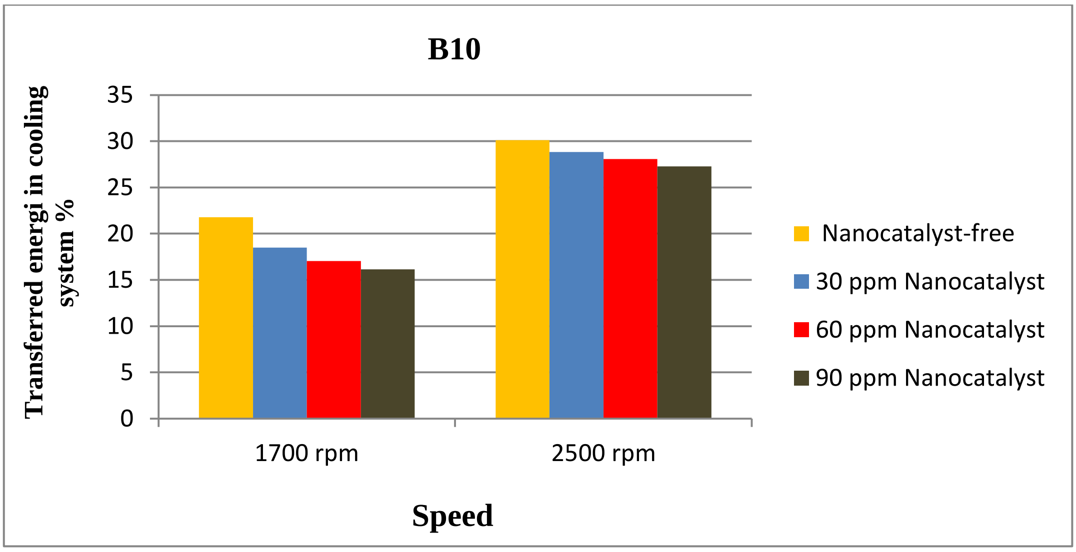

Fig.6. Analysis of the energy transferred into the cooling system for different nano-catalyst concentrations and B10 fuel blend

Incomplete combustion causes more emission and leaves more deposits in the combustion chamber. This deposit leads to the formation of carbon deposits on the combustion chamber's walls. Those carbon deposits increase the temperature in the combustion chamber as well as NO_x emissions.

Cerium oxide and molybdenum oxide can prevent the oxygen that leads to complete combustion and lower emission because of an increase in the amount of oxygen (Eqs. (7) and (8)).

$$2CeO_2 \leftrightarrow Ce_2O_3 + \frac{1}{2}O_2 \qquad (7)$$

$$2MoO_3 \leftrightarrow 2MoO_2 + O_2 \qquad (8)$$

The logic of using cerium oxide and molybdenum oxide as a catalyst, which allows the above-mentioned reaction and easily occurs in exhaust gases, is the low redox potential of Ce^{3+} and Ce^{4+}, and also Mo^{4+} and Mo^{6+} [12–26].

Equations (9–12) show that cerium oxide and molybdenum oxide supply oxygen to reduce carbon monoxide (CO), hydrocarbons (HC), and soot production by preparing the required oxygen to oxidize hydrocarbons and carbon monoxide respectively.

$$(2x+y)CeO_2 + C_xH_y \leftrightarrow \left\{\frac{(2x+y)}{2}\right\} Ce_2O_3 + \frac{x}{2}CO_2 + \frac{y}{2}H_2O \qquad (9)$$

$$(2x+y)MoO_3 + C_xH_y \leftrightarrow \left\{\frac{(2x+y)}{2}\right\} MoO_2 + \frac{x}{2}CO_2 + \frac{y}{2}H_2O \qquad (10)$$

$$2CeO_2 + CO \leftrightarrow Ce_2O_3 + CO_2 \qquad (11)$$

$$2MoO_3 + CO \leftrightarrow MoO_2 + CO_2 \qquad (12)$$

Equations (13) and (14) display the oxygen absorption of cerium oxide and molybdenum oxide, which causes a decrease in the production of NO_x.

$$Ce_2O_3 + NO \leftrightarrow 2CeO_2 + \frac{1}{2}N_2 \qquad (13)$$

$$MoO_2 + NO \leftrightarrow MoO_3 + \frac{1}{2}N_2 \qquad (14)$$

According to Eqs. (9–14), the nano-particles of cerium oxide and molybdenum oxide, as a catalyst, could decrease the production of NO_x emissions and lead to a reduction in the peak temperature in the combustion chamber [22]. They can also provide oxygen molecules, which cause complete combustion and decrease the amount of carbon monoxide and unburned hydrocarbon. Because of these two mechanisms in the cylinder, the energy transferred to the cooling system for the blends containing the nano-catalyst as an additive decreased in comparison with the nano-catalyst-free counterpart.

3.3.Energy transferred into exhaust gases and unaccounted heat loss

Lower energy transfer into exhaust gases was achieved at all three concentrations of 30, 60, and 90 ppm for both B5 and B10 in comparison with the base fuels (Figs. 7 and 8).

It can be comprehended from Fig.7 that compared with the nano-catalyst-free B5, the addition of a nano-catalyst at 30, 60, and 90 ppm resulted in 0.5%, 1.1%, and 1.51% reduction of the energy transferred to exhaust gases at 1,700 rpm, and 1.02%, 1.43%, and 2.26% at 2,500 rpm for B5.

It is obvious from Fig.8 that compared with the nano-catalyst-free B10, the nano-catalyst at 30, 60, and 90 ppm leads to 0.13%, 0.7%, and 1.41% reduction in transferred energy in exhaust gases at 1,700 rpm, and 1.5%, 2.46%, and 2.62% at 2,500 rpm for B10.

According to Eqs. (9–14), the concentration of NO_x, CO, and HC decreased with the use of a nano-catalyst in fuel blends. Lower CO, HC, and NO_x emissions are responsible for the lower energy transfer to exhaust gases, which is the result of the lower exhaust gas temperature.

Also, as discussed earlier, using cerium oxide and molybdenum oxide as the catalyst

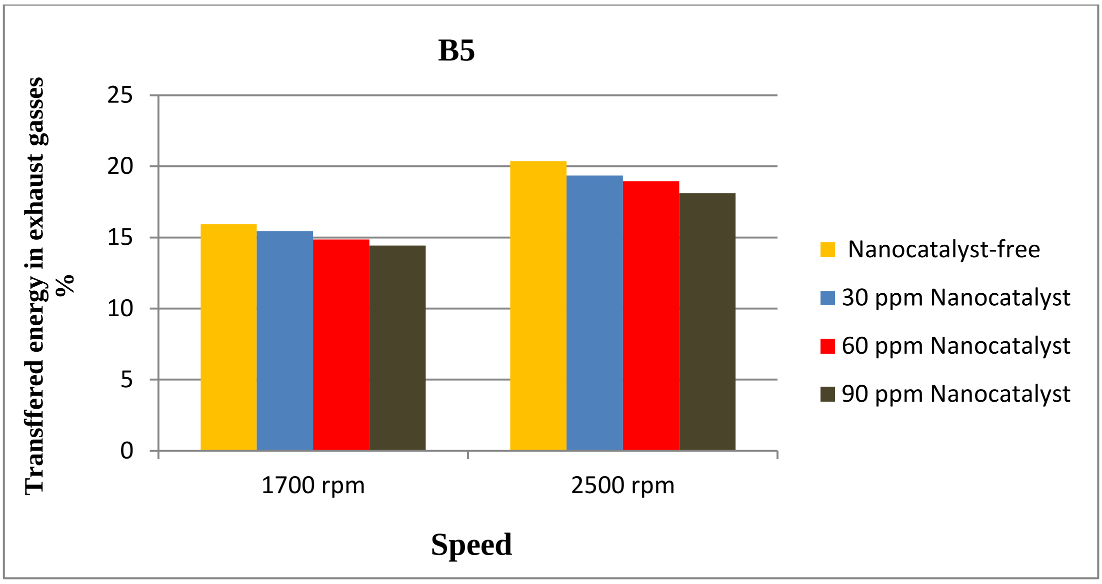

Fig.7. Analysis of the energy transfer to exhaust gases for different nano-catalyst concentrations and B5 fuel blend

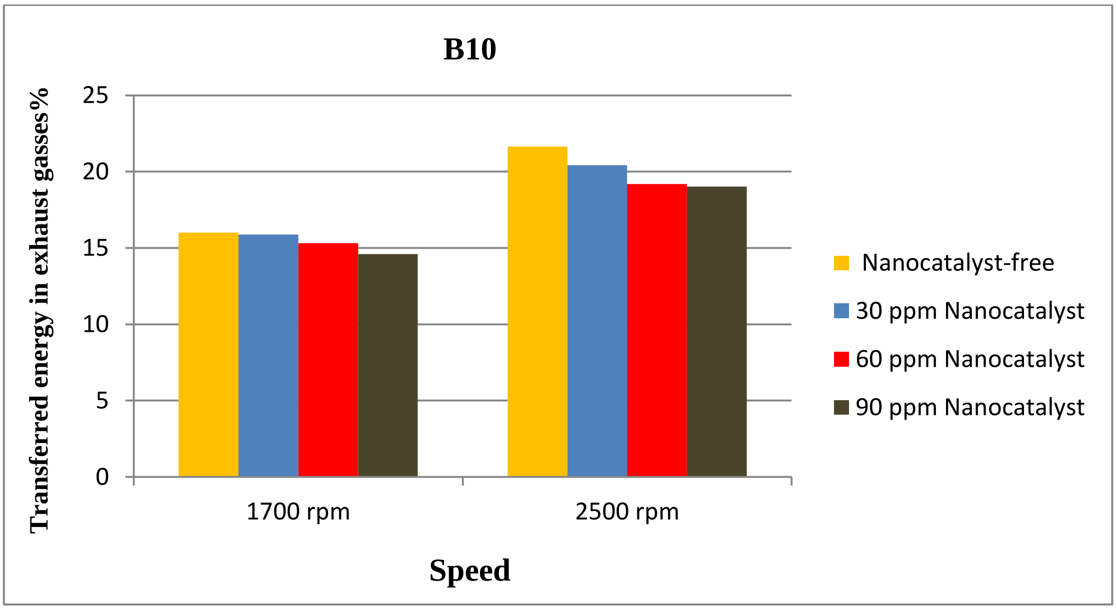

Fig.8. Analysis of energy transfer to exhaust gases for different nano-catalyst concentrations and the B10 fuel blend

in fuel blends causes a decrease in the peak temperature of the combustion chamber. The lower temperature in the combustion chamber brings about the reduction in the exhaust gas temperature.

Finally, the unaccounted heat loss, which mostly included the lubricating oil heat loss, the convection and radiation heat losses from the cylinder walls, and the other heat losses from the engine were calculated by deducting the supplied fuel energy from the overall heat loss [2]. The trend of the unaccounted heat loss was not clear and definite. Other researchers also reported this trend of heat loss [1, 20, 33].

4.Conclusions

The thermal balance of diesel-biodiesel blends (B5 and B10) with the addition of the hybrid catalyst (CeO_2-MWNCTs and MoO_3-MWNCTs) at 30, 60, and 90 ppm was investigated on a single-cylinder diesel engine at two speeds (1,700 and 2,500 rpm).
The conclusions are drawn as follows:

1- The thermal efficiency of B5 and B10 increased with the inclusion of a nano-catalyst in the fuel blends. The highest increase in thermal efficiency was observed at 6.75% for $B10_{(90\ ppm)}$ at 1,700 rpm. The supply of oxygen by CeO_2 and MoO_3 nano-particles in a chain reaction played a vital role in increasing the thermal efficiency because of complete combustion.
2- CeO_2 and MoO_3 nano-particles decreased the peak temperature in the combustion chamber and supplied oxygen to reduce the CO and HC emissions. By using a nano-catalyst at 30, 60, and 90 ppm concentrations, the air heat loss decreased for the energy transfer to both the cooling system and the exhaust gases. The maximum reduction in air heat loss and exhaust heat loss were observed to be 5.61% for $B10_{(90\ ppm)}$ at 1,700 rpm and 2.62% for $B10_{(90\ ppm)}$ at 2,500 rpm respectively.

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