

Application of CuO nanoparticles on performance and emission characteristics of ternary blends of diesel, waste cooking oil and pumpkin seed oil biodiesel in an IC engine

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Received 18 October 2024; accepted 6 January 2025

The aim of this work is to demonstrate the effect of copper oxide (CuO) nanoparticles doped biodiesel on the performance and emission characteristics of a compression ignition (CI) engine. The base fuel (B20) is a ternary blend of 10% waste cooking oil (WCO) biodiesel, 10% pumpkin seed oil (PSO) biodiesel, and 80% conventional diesel. The B20 blend has been doped with CuO nanoparticles at four different dosage of 20, 40, 60 and 80 ppm. The tests are conducted on a single-cylinder diesel engine with no modifications and under standard operating conditions. WCO and PSO were identified for this work due to their good economic viability, and the oils are converted into biodiesel through the transesterification process. The performance parameters, such as brake thermal efficiency (BTE) and brake specific fuel consumption (BSFC) under different load conditions are evaluated. The emission characteristics of carbon monoxide (CO), hydrocarbons (HC), and oxides of nitrogen (NO_x) are also considered for this study. From the results, it is found that the use of a ternary blend with CuO for an IC engine gives higher BTE with reduced BSFC. It is also perceived that the emission of CO and HC from the engine can be controlled with the addition of CuO nanoparticles.

Keywords: Biodiesel, Compression ignition engine, Emission characteristics, Non-edible oil, Ternary blend

Introduction

Internal combustion (IC) engines are machines utilized for energy conversion, particularly in the transportation sector. The automotive industry is continuously developing with advanced technologies, but at the same time, numerous ecological issues related to its use are becoming more serious¹. Much effort is being concentrated on combustion technology to increase the performance and reduce the consumption of fossil fuels. Reduction of pollutants from IC engine is an important one, since the elevated levels of pollution observed in urban areas pose health risks to humans and all living organisms². Due to its widespread utilization in all industries, fuel for IC engines is always in demand globally³. In order to fulfill the demand, the majority of research focused on renewable energy sources⁴. The most significant role in biodiesel research has been played by plant-based oils, which are utilized for a variety of applications, such as automobiles, ships, power generations and others. Biofuels have the ability to improve environmental stability by lowering

greenhouse gas emissions⁵. They can also aid in the protection of ecosystems and natural resources. Biofuels have the potential to improve energy security and lessen global dependency on fossil fuels. It can offer a low-carbon transportation option, particularly for large trucks, ships, and aircraft. Compared to diesel, biodiesel is a green energy source that has less aromatic and sulphur content, as well as a higher flashpoint, a cetane number and lubricity⁶. Reduced oxidation stability, higher pour point, viscosity and lesser heating value are some of the drawbacks of biofuel. Many researchers have produced and utilized biodiesel from different non-edible oils for engine operations⁷. From these experiments, it was noted that the biodiesel-fueled engines produce less emissions than diesel-fueled engines, but there is a small surge in nitrous oxide (NO_x) emissions⁸. However, it was not advised to use 100% biodiesel for IC engines. As a result, under controlled laboratory conditions, biodiesel and diesel were combined in specific amounts. The choice of oil for biodiesel production is heavily influenced by many

factors, including availability, cost, and production methods⁹. Recently, there has been a lot of worry about the use of edible oils for IC engine operations since they compete with food ingredients. As a result, the usage of non-edible oils for energy purposes is recommended¹⁰.

A significant portion of the price of biodiesel production depends on raw materials. Usage of low-cost raw materials is one technique to minimize the cost of production. Finding less expensive, non-edible oils is a main objective for biodiesel generation¹¹. As a result, waste cooking oils and non-edible oils have attracted increased interest as feedstock for the generation of biodiesel¹². In this series, WCO and PSO are recommended as raw materials for biodiesel. Disposal of used cooking oil into the environment primarily affects the quality of the land and groundwater¹³. Repeated use of cooking oil for food production beyond certain standards is carcinogenic. It is a cause of obesity and various health diseases¹⁴. Due to the availability of WCO, the researchers working on alternative fuel have pushed the production of biodiesel for IC engine operations. The converted WCO biodiesel through the transesterification process has many advantages over conventional diesel, including a higher cetane index and a lower sulphur level. Without any structural change, biodiesel can be used for engine operation. Yu *et al.* reported the effects of engine emission and combustion using WCO biodiesel¹⁵. The authors tested the biodiesel in an IC engine and exposed it to higher peak pressure than diesel fuel and they found coke-like deposition inside the chamber, and the oil they investigated had emissions rates higher than diesel. Experimental research on the use of WCO biodiesel was directed by Rao *et al.*¹⁶. Through an experimental study, the authors found a higher in-cylinder pressure and a higher heat release rate (HRR). In terms of performance, the WCO biodiesel showed lower BTE due to the poor heating value. The experimental work on IC engines using WCO biodiesel conducted by Pauline *et al.* showed increased power output with decreased fuel consumption and emissions¹⁷. The basic properties of the fuel revealed that it complied with biodiesel regulations. Under partial load conditions, the output and emission analysis were done at compression ratios of 14:1 and 16:1. The WCO in the engine showed reduced BTE with increased SFC¹⁸. The experimental results showed 21.75% reduction in CO with a minor increment in CO₂ and NOx. In comparison to other types of vegetable oils, PSO has a price advantage. Since it is not frequently used as edible oil, the seeds contain approximately 45% oil, giving them a significant advantage over other

vegetable oils¹⁹. PSO biodiesel has been utilized for IC engine operation by various authors in various countries²⁰⁻²². From this collected works, it was established that the usage of PSO biodiesel can limit the emission of harmful gases from the engine.

Biodiesel with nanoparticles are novel class of fuel that uses nanoparticles as additives to lower emissions while improving engine performance²³. According to Javed *et al.* nanoparticles have the capability to improve volumetric energy density of fuels, which in turn has the potential to reduce ignition lag by improving heat transfer²⁴. When aluminium oxide nanoparticles were added to tamarind seed biodiesel, Raju *et al.* noticed an increased BTE and decreased CO and HC emissions²⁵. With titanium oxide nanoparticles, palm oil biodiesel showed considerable progress in cetane number and calorific value²⁶. The experimental study combined with water-diesel emulsion and aluminium oxide nanoparticles showed effective combustion^{27,28}. The effective combustion of the fuel is due to its fast evaporation. During the experiment, it was also noted that the engine operated smoothly with reduced noise. According to Mirzajanzadeh *et al.* nanoparticles dispersed in the biofuel increased favourable fuel properties, including calorific value²⁹. It is also a guide to proper atomization, vaporization and air-fuel mixing³⁰. For the TV1 type Kirloskar engine, Thirugnanam *et al.* used nickel oxide (NiO) nanoparticles with palmyra oil biodiesel³¹. The study found that a NiO-dosed with B20 resulted in 1.3% improved BTE. The results of the emission analysis showed reduced CO and HC productions by 12–22% and 18–24%, respectively. However, the nanoparticles with biodiesel slightly increased NOx emissions. Tewari *et al.* explored the effects of carbon nanotubes in honge oil-derived biodiesel³². The biodiesel with nanotubes improved BTE and NOx production while minimizing CO and HC.

It is evident that very few authors have looked into ternary biodiesel blends with nanoparticles for IC engines. In the current work, ternary blends of two distinct biodiesels were produced from WCO, PSO and diesel for IC engine operation. The ternary blended fuel was mixed with CuO nanoparticles to assess engine operating characteristics. Analysis and comparison were done on the experimental data for BTE, SFC, CO, HC, and NOx emissions.

Experimental Section

Oil collection and extraction

The WCO used for this work was gathered from a local restaurant in Coimbatore, India. It is a collection

of waste palm oil used for frying purposes. In order to maintain uniform properties, the required amount of WCO was collected at a single time and stored separately. PSO is not available on the market because it is not currently produced commercially. Therefore, the required quantity of seeds was collected and further processed to obtain the required quantity of PSO. The seeds were gathered and exposed in sunlight for a month to dry them. Several methods, including hydraulic pressing, solvent extraction could be used to extract oil from the seeds. According to our earlier research, solvent extraction was considered as the most effective one to extract oil from the seeds³³. In addition, this approach is less expensive. Therefore, the oil from pumpkin seeds was extracted via soxhlet extraction method.

Biodiesel production

The methyl esters of the oils were prepared using the transesterification process. For that, the stoichiometric oil-to-alcohol ratio was found to be 6:1. The weight of NaOH was calculated to be 1% of the oil. Methyl alcohol and NaOH were combined to create a 100 ml methoxide solution. Using a magnetic stirrer, 500 mL of WCO was placed in a bottle and blended at 400 rpm and 60°C. The produced solution was poured onto the oil. A thermometer was set at 60°C. The process was continued for up to 60 min with the formation of glycerin and biodiesel. The phase separation process was then finished after 6 h of standing time. The separating funnel was clear of the glycerin phase, even though the biodiesel was found with a minor amount of glycerin, salt and methanol. These chemicals were separated and purified from the biodiesel using a washing procedure. Finally, the waste cooking oil methyl ester (WCOME) was obtained and stored in a separate glass column. The

procedure was repeated for pumpkin seed oil methyl ester (PSOME). Nearly 81% of the biodiesel was produced for WCOME, and 93% for PSOME. The physiochemical characteristics of both biodiesels were found and reported in Table 1.

Ternary blend production

Due to higher free fatty acids (FFA), WCO and PSO cannot be used directly for engine analysis. The prepared methyl esters had good atomization properties. The specified oils are widely accessible. Consequently, there is a feasibility to combine WCOME and PSOME with petroleum fuel. By directly combining, the ternary blends are created. For engine analysis, the B20 blend was made by combining 80% diesel and 10% of each biodiesel.

Preparation of nano biodiesel

For engine operation, four types of nanofuel were prepared and represented as BxCy (x represents volume fraction and y represents ppm). For example, B20C20 (B20-20% biodiesel, 80% diesel and C20-20 ppm CuO). The homogeneous B20C20, B20C40 and B20C60 B20C80 (different dosages of 20 ppm, 40 ppm, 60 ppm, and 80 ppm) fuels were prepared using an ultrasonicator. The nano CuO was supplied by M/s. Sigma-Aldrich, USA. This study is limited to the usage of B20 since it shows similar readings of diesel during the trial experiment. Therefore, the nano particles at different dosages were mixed with B20. The properties of the tested fuel are recorded in Table 2. Compared to standard diesel, B20C80 has greater calorific value.

Engine set up

A single-cylinder, direct-injection, water-cooled diesel engine was employed for this work. Table 3 displays the specifications of the test rig. The engine is

Table 1 — Properties of the biodiesel

Properties	WCOME	PSOME	Unit	Test standard
Density	852	895	kg/m ³	ASTM D 1798
Kinematic viscosity	3.94	5.8	cSt	ASTM 445
Flash point	142	174	°C	ASTM D 93
Cetane index	57	54	-	ASTM D 613-84
Calorific value	37.82	40.70	MJ/kg	ASTM D 240

Table 2 — Fuel properties

Properties	B20	B20C20	B20C40	B20C60	B20C80	Diesel	Unit
Density	819	823	824	825	827	815	kg/m ³
Kinematic viscosity	2.95	3.14	3.14	3.16	3.18	2.90	cSt
Flash point	65	66	67	67	68	59	°C
Cetane number	52	54.1	54.3	54.9	55.1	51	-
Calorific value	42.90	43.10	43.35	43.55	43.70	43.60	MJ/kg

Table 3 — Engine specification

Brand	Kirloskar
Model	TV1
Number of cylinder	1
Compression ratio	17.5:1
Rated power	5.2 kW
Rated speed	1500 rpm
Number of stroke	4
Cooling type	Water
Stroke	110 mm
Bore	87.5 mm
Injection pressure	210 bar
Fuel timing	23 °BTDC
Peak pressure	77.5 kg/cm ²
Gas analyzer	AVL DiGas
Loading	Eddy current dynamometer

mated with an alternator and then to a load bank. For all the trials, the engine was operated at 1500 rpm. For every fuel, the load was increased from 0 to 100% with five equal distributions of 20%, 40%, 60%, 80% and 100%. Initially, the engine was ran with diesel and then operated in biofuel mode. The readings were noted after the coolant and oil temperatures had stabilized. The emissions were recorded with the aid of AVL DiGas 44 (AVL India private limited). Fig. 1 displays the graphical representation of the experimental setup.

Results and Discussion

Variation in brake thermal efficiency

The BTE demonstrates how effectively the fuel's energy may be transformed into mechanical energy. The difference in BTE according to engine load is depicted in Fig. 2. It is obvious that the BTE of the engine rises as the load increases from 0% to 100%, and the BTE for B20 is the lowest among all the tested fuels. For higher biodiesel blends, the calorific value of the fuel decreases, and fuel consumption increases. The viscosity of the blend is high, which can lead to poor atomization³⁴. For example, the B20 blend has a higher viscosity of 2.95 cSt than diesel (2.90 cSt), which results in a lower BTE. The physical delay is shortened by the inclusion of nanoparticles with the blended fuel, which also shortens the evaporation duration. The higher thermal conductivity of the nanoparticle results in higher heat transfer rates during the delay period and starts early combustion. The lower efficiency with B20 under all loads is due to the higher density, improper mixing and low heat transfer. Thus, the efficient energy use using nanomaterials was made potential, which increased the engine efficiency. Under maximum load condition the BTE of the engine at B20, B20C20, B20C40, B20C60, B20C80 and diesel was 31.12, 32.68, 33.86, 35.78,

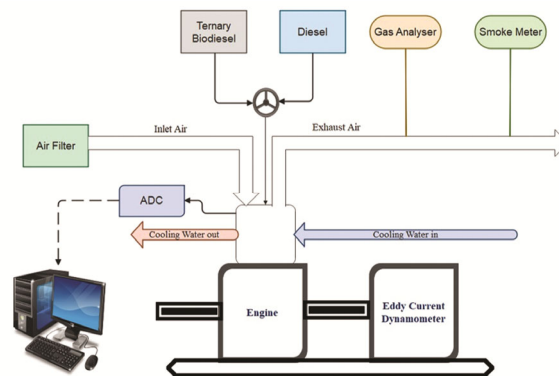


Fig. 1 — Schematic of the experimental setup

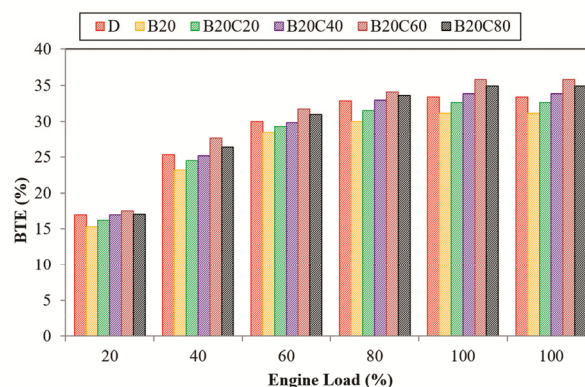


Fig. 2 — Variation in BTE

34.91 and 33.42%, respectively. Compared to B20 and diesel, B20C60 showed 13.02% and 6.6% more efficiency at 100% load conditions. At maximum load, 5.01%, 8.8% and 12.18% of the increment were recorded for B20C20, B20C40, B20C80, respectively, compared to B20. Improved combustion inside the chamber is caused by increased oxygen levels in the fuel, improved evaporation, and a higher surface-to-volume ratio in nanofuel^{35, 36}. The BTE increased up to the dosage of 60 ppm CuO, and the value decreased beyond that level. The higher viscosity may be the reason of the decreasing efficiency with higher dosage³⁷. Compared to other combinations, B20C60 showed better results. The increased nanoparticle dosage might enhance the momentum of the nanofuel and reduce turbulence, which could result in improper fuel mixing and incomplete combustion, which could cause a significant drop in performance³⁸.

Variation in BSFC

The impact of CuO nanoparticle addition to B20 on BSFC is depicted in Fig. 3. At 1500 rpm speed, the biodiesel with 20 ppm, 40 ppm and 60 ppm CuO consumed less fuel than B20 under all load conditions,

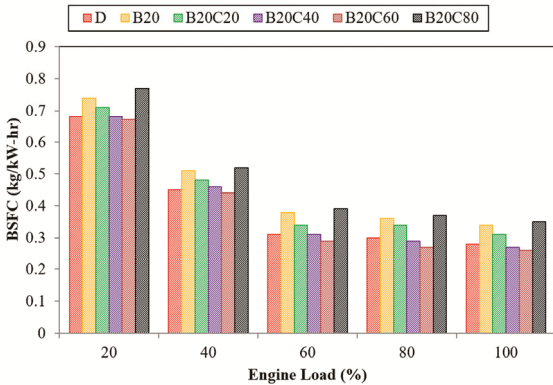


Fig. 3 — Variation in brake specific fuel consumption

while B20C80 consumed more fuel than all other tested fuels. At 100% load, B20, B20C20 and B20C80 consumed more fuel than diesel. When compared to other concentrations, B20 biodiesel with 60 ppm CuO has improved combustion characteristics. This combination consumed a lower quantity of fuel due to improved quality and a shorter ignition delay³⁹. The density is improved in biodiesel-diesel fuel, which lowers the heating value of biodiesel blends⁴⁰. In general, adding CuO improves combustion, increases power, and decreases BSFC. At 100% load conditions, the BSFC for B20, B20C20, B20C40, B20C60, B20C80 and diesel are 0.28, 0.34, 0.31, 0.27, 0.26 and 0.35 kg/kW-h, respectively. In comparison to B20, engines operating at B20C20, B20C40, and B20C60 showed 8.82%, 20.59%, and 23.53% reduced BSFC, respectively, and in comparison to diesel, engines operating at B20C40, B20C60 showed 3.57% and 7.14% reduced SFC. The fuel-containing nanoparticles can act as an oxygen donor during combustion⁴¹. Shaisundaram *et al.* have reported the same behaviour under cerium oxide nanoparticles⁴².

Variation in CO emission

Fig. 4 shows the differences in CO emissions caused by changes in loading rates for diesel, biodiesel and nanofuel. With increased load, the CO production level continuously increases. This is caused by the variations in air-fuel ratio⁴³. The existence of carbon and oxygen at the level of combustion are the major reasons for the development of CO during combustion. When a fuel is burned, the carbon in it releases CO, which is then transformed into CO₂. If there was less oxygen available, the incomplete combustion resulted in more CO⁴⁴. At partial and full load operating conditions, the concentration of CO emitted from the engine is low for

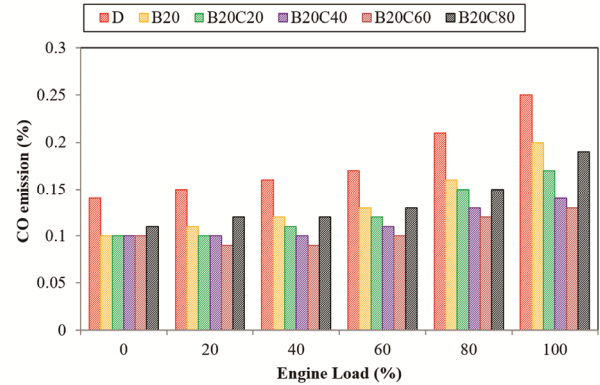


Fig. 4 — Variation in CO emission

all biodiesel. This phenomenon is connected to the concentration of oxygen and the higher cetane number⁴⁵. These findings demonstrate that CO emission is significantly decreased when the nanoparticle content is increased. The mechanism is ascribed to the addition of CuO encouraging the conversion of CO into CO₂⁴⁶. The wide surface contact areas of the CuO nanoparticles used in this study increase chemical reactivity and decrease the ignition delay dramatically. The ignition delay can be shortened to optimize the combustion process. As a result, CO has decreased⁴⁷. CO emissions at full load for B20, B20C20, B20C40, B20C60, and B20C80 and diesel are 0.25, 0.20, 0.17, 0.14, 0.13, and 0.19%, respectively. The concentration of CO in emitted gas is associated with the amount of OH radicals present during combustion. More CO is reduced as a result of more OH radicals produced with higher CuO concentration. In this study, at 80 ppm dosage level, the OH radical is at its minimum, causing lower CO reduction. A similar trend was observed with rapeseed biodiesel⁴⁸.

Variation in HC emission

Fragments of partially burned fuel is the reason for the development of HC emissions. Due to higher oxygen available in biodiesel, numerous researchers discovered that biodiesel-diesel blend results in thorough combustion⁴⁹. The addition of nanoparticle can dramatically lower the formation of unburned hydrocarbon. Higher cetane index and amount of relative air-fuel ratio of biofuel reduce the ignition delay, which drops higher production of HC⁵⁰. The oxygenated additive in the CuO nanoparticles promotes complete combustion compared to diesel. Fig. 5 exemplifies the variation in HC emissions as a function of load. Similar to CO emission, a rise in load causes an increase in HC emission. For all load condition, the lower and higher HC production was

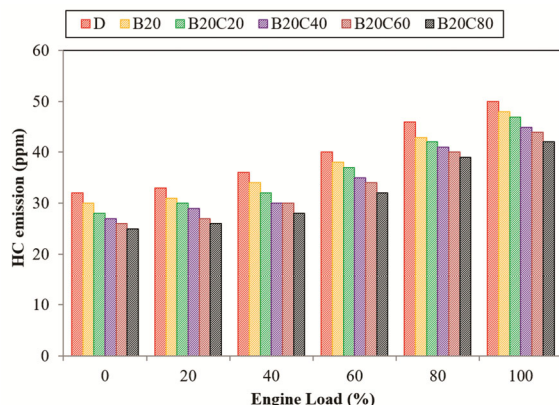


Fig. 5 — Variation in HC emission

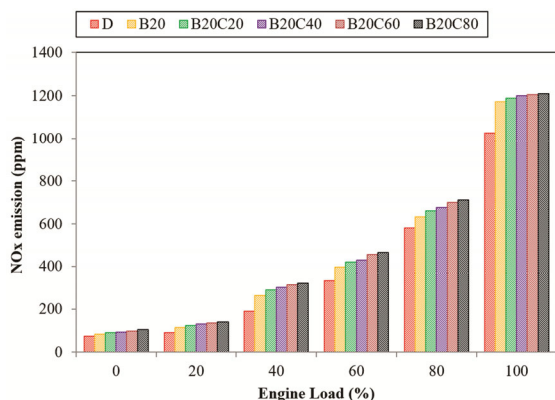


Fig. 6 — Variation in NOx emission

note down for diesel and B20C80, respectively. From Figure, the mean HC emissions of B20, B20C20, B20C40, B20C60, B20C80 and diesel were 48, 47, 45, 44, 42 and 50 ppm, respectively. Compared to diesel, the reduction of HC for the above fuel blend at 100% load is 4, 6, 10, 12 and 16%. In this study the maximum reduction of HC was noted with 80 ppm CuO. The diesel at higher load burn partially leads to the emission of higher HC.

Variation in NOx emission

NOx emissions are caused by nitrogen oxidation at high temperatures. Fig. 6 portrays the difference in NOx emissions. The emission of NOx is a role of temperature of the cylinder. At elevated combustion temperature, the process is closer to stoichiometric and leads to NOx production⁵¹. The production of NOx is observed as an increasing trend with increased load. With increased load, the temperature of the chamber also increases, resulting increased NOx. For all loads, the use of biodiesel showed increased NOx emissions due to higher oxygen inside the cylinder. The thorough combustion increased the temperature of the chamber. It is noted that the NOx production for diesel is very

minimum related to other tested fuels. The NOx is further increased with the increased dosage level of CuO with biodiesel-diesel blend due to higher pressure and temperature⁵². At 100% load condition, the value of NOx in the exhaust showed 1172, 1189, 1201, 1204, 1210 and 1026 for B20, B20C20, B20C40, B20C60, B20C80 and diesel, respectively. Similar trends were also reported by the literature^{53,54}. The increased NOx from engine exhaust can be controlled by selective catalytic reduction (SCR) to alter NOx into nitrogen. Moreover, a few other process modifications including low-NOx burners, reburning, combustion staging, gas recirculation, water injection, and low excess air firing can lessen engine NOx emissions.

Conclusion

In this study, engine tests were conducted with the blends of waste cooking oil biodiesel, pumpkin seed oil biodiesel and diesel with CuO. Physical and chemical characteristics of the blends have been found. The tests were carried out from no load to full load, and the corresponding performance and emission characteristics were compared to diesel. With the addition of CuO to the B20 ternary blend, BTE was found to be increased by 13.02%. This improved BTE demonstrates the occurrence of catalytic activity by the nanomaterial. Also, the reduction in BSFC compared to the ternary blend for B20 with the dosage of 20, 40 and 60 ppm was 8.82%, 20.59% and 23.53%, respectively. The use of a ternary blend with CuO was much more helpful in reducing CO and HC emissions compared to diesel. It was also found that NOx emissions decreased dramatically. Thus, changing the engine operating parameters can improve engine performance and reduce harmful emissions.

Nomenclature

D	Diesel
WCO	Waste cooking oil
PSO	Pumpkin seed oil
WCOME	Waste cooking oil methyl ester
PSOME	Pumpkin seed oil methyl ester
IC	Internal combustion
CI	Compression ignition
CuO	Copper oxide
B20	10% WCOME +10% PSOME +80% D
B20C20	B20+20 ppm CuO
B20C40	B20+40 ppm CuO
B20C60	B20+60 ppm CuO
B20C80	B20+80 ppm CuO

ASTM	American society for testing and materials
VCR	Variable compression ratio
BTE	Brake thermal efficiency
BSFC	Brake specific fuel consumption
CO	Carbon monoxide
HC	Hydrocarbon
NO _x	Oxides of nitrogen
ppm	Parts per million

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