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Influence of Waste Cooking Oil Methyl Ester Biodiesel Blends on the Performance and Emissions of a Diesel Engine

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Abstract The present study deals with the performance and emissions of conventional diesel fuel and biodiesel produced from waste cooking oil and their blends (B10, B15). The waste cooking oil methyl esters synthesis has been (WCOME) carried out by a single step alkali catalysed transesterification reaction. Significant physicochemical properties have been measured and compared against the ASTM D6751 standards. The tests have been performed on a single cylinder, direct injection diesel engine at a constant speed 1500 ± 50 rpm. During the tests, brake thermal efficiency, specific fuel consumption, exhaust gas temperature, exhaust emissions are measured. The experimental results revealed that, relative to diesel, WCOME fuel blends show 1.7–4.14 % decrease in the brake thermal efficiency and 2.18–5.57 % increase in the brake specific fuel consumption due to higher density and kinematic viscosity of WCOME, which reduces the fuel atomization rate. Moreover, most of the constituents of exhaust gas such as CO (13.67–16.89 %) and HC (4.35–11.84 %) along with greenhouse gas such as CO_2 (8.34–17.39 %) are reduced in case of all the blends. However, an increase in the NOx emissions (0.3–4.2 %) is mainly due to the higher cetane number of fuel blends, which decreases the ignition delay. The results of this study revealed that WCOME blends show fewer exhaust emissions with a little compromise in the performance of the engine.

Abbreviations

B0, B5	Blend 0 %, blend 5 %
BP	Brake power
BSFC	Brake specific fuel consumption
bTDC	Before top dead centre
BTE	Brake thermal efficiency
CNG	Compressed natural gas
CO	Carbon monoxide
CO_2	Carbon dioxide
CR	Compression ratio
EGT	Exhaust gas temperature
FFA	Free fatty acids
HC	Unburnt hydrocarbon
IC	Internal combustion
LPG	Liquefied petroleum gas
NMR	Nuclear magnetic resonance
NOx	Oxides of nitrogen
WCO	Waste cooking oil
WCOME	Waste cooking oil methyl esters
^{1}H NMR	Hydrogen 1 nuclear magnetic resonance

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Introduction

Fuels are essential input for economic development, social growth, human benefit and quality life of every country. Currently, most of the world's energy demands are rendered by fossil based resources, such as gasoline, kerosene,

diesel and natural gas etc. Since 1970, need for energy is increasing with the development of technology, with an increasing trend of modernization, rapid population growth and industrialization; consequently, the world's energy need is also growing at a faster rate [1, 2]. Furthermore, fossil derived fuels are producing negative effects on the environment and burning of these fuels contributes discharge of pollutant gases like NOx, CO_2, SOx, HC [3]. However, currently human beings are caught between two major crises due to rapid depletion of fossil fuels and degradation of the eco-system. Internal Combustion (IC) engines (both diesel and petrol engines) have fallen victim to these crises. Due to the aforementioned and following understandings, like uncertainties in the petroleum supply, a result of greenhouse gases from industries, increased environmental concern and their high prices have accelerated an intensive exploration of substitute sources for fossil-based fuels, including diesel fuel [4]. Nabi et al. [5] reported that within 40 years, the present stock of fossil fuels will exhausts at an increased consumption rate approximated to be 3 % per annum. Therefore, it is essential that low emission alternative fuels must be developed to use in diesel engines in order to meet the current energy demands. In addition to that, for arising economy, it is understood that the energy uptake must be much more than the level at present.

Currently, various potential substitutes of fuels are available such as plant seed oils, alcohols (methanol, ethanol and butanol), producer gas and liquefied petroleum gas (LPG), gases such as compressed natural gas (CNG) etc. Among these available resources, plant seed oils provide a promising substitute to conventional diesel engines since they don't contain sulphur, aromatic hydrocarbons, metals, oil residues. Similarly, they also can maintain carbon neutrality, provides good physico-chemical properties and vegetable oils can be transformed easily into the modern forms of energy. Many researchers have concluded that vegetable oils hold promise as an alternative to diesel fuel, since their properties are close to the diesel fuel [6, 7]. Recently, the use of biodiesel has grown dramatically around the globe. However, utilizing raw vegetable oils for diesel engines can cause numerous engine-related problems such as engine deposits, injector chocking and piston ring sticking due to the increased viscosity and low volatility of vegetable oils [8–10]. Nevertheless, these negative consequences can be reduced via transesterification of vegetable oil to form fatty acid esters [11–14]. Transesterification reduces the viscosity of vegetable oil and supplies a fuel having viscosity near to that of No. 2 conventional diesel fuel. Transesterification is a process in which triglyceride reacts with short-chain alcohol in the presence of a catalyst to produce fatty acid esters and glycerol. Transesterification technique also used to minimise the product cost, and it improves the physico-chemical properties of fatty acid esters in order to use in diesel engines.

Currently, raw materials for more than 95 % of biodiesel production come from edible oils (i.e. rapeseed, palm, canola, mustard, peanut and soybean). The consumption of these raw materials is due to their abundance around the globe in many regions. In addition to that, the properties of biodiesel produced from plant seed oils are worthy to be used as a conventional diesel fuel substitute. However, utilisation of plant seed oils to synthesise biodiesel is not viable in view of a large gap in demand and supply of such oils for food, and they are high-priced to be utilized at present. Therefore, the use of non-edible plant seed oils compared to edible seed oils is very significant in order to reduce the raw material cost and proper utilization of non-edible, edible waste oils, which are abundantly available in the commercial way. Since the cost of feed stock accounts for 60–80 % of the total price of methyl esters production, properties of fatty acid esters produced from various feed stocks are quite different, hence selecting a proper feed stock plays a major role in the entire synthesis process [15, 16]. In order to overcome the aforementioned difficulties many technocrats, industrialists as well as scientists are attracted towards edible waste, non-edible oil sources, which are unfit for the edible purpose due to the presence of few toxic constituents. Further, in-edible plant seed oil crops can be cultivated in barren lands that are unfit for food crops and the cost of cultivation is much lower, because these crops can still maintain higher oil yields without intensive care. Indeed, most of the non-edible oils hold high free fatty acids (FFA) content, thus these non-edible oils need multiple chemical steps to synthesise biodiesel, which increases the production cost and lower the ester yield. Therefore, in the current study methyl esters is synthesised from waste cooking oil (WCO) having very low FFA content.

During the past decade biodiesel has been broadly investigated in testing different types of engines. Many studies on engine test reported a reduction in particulate matter (PM), carbon monoxide (CO), and total hydrocarbon (THC) emissions with either neat or blended biodiesel compared to diesel fuel [17]. Wide range of studies has been conducted on combustion characteristics and regular emissions of a diesel engine fueled with biodiesel obtained from WCO [18–20]. Previous investigation results revealed that, biodiesel has higher viscosity compared to conventional diesel fuel; therefore in order to use the prepared biodiesel in DI engine it should be blended with conventional diesel. Hence, the effect of blending ratio on the mixture should be determined to reduce the emissions and safe operation of the engine. However, vast literature is available about the influence of using biodiesel in pure

form or biodiesel blends with conventional diesel fuels, but there is no similarity in many engine aspects. For this reason, there is a necessity to perform a set of experiment before using any biodiesel from any resource in DI engine that has not been documented. In this direction, present work aims to study the influence of biodiesel blending ratio on engine performance (brake thermal efficiency, specific fuel consumption, exhaust gas temperature, exhaust emissions) and emission characteristics (CO, HC, CO_2 and NO_x) at a wide range of engine operating conditions. All the experiments are performed without any engine modification and this data will be important in formulation of optimal biodiesel blends and their use in DI engines from waste/used cooking oils.

Materials

The WCO used in this study (fish fried soybean oil) has been collected from the institute hostel mess, IIT Guwahati, Guwahati, India. Methanol, phenolphthalein Indicator, sodium hydroxide (NaOH) pellets, ethyl alcohol, carbon tetrachloride (CCl_4), potassium Iodide (KI), sodium thiosulphate ($Na_2S_2O_3$), Wij's reagent, hydrogen peroxide, potassium hydroxide are supplied by Merck India Pvt. Ltd. All the other reagents used for analysis are analytical grade and are used as received without any further purification.

Experimental Methodology

Synthesis of WCO Biodiesel, Blending with Diesel and Physico-Chemical Characterization

WCO biodiesel is prepared by a single step alkali catalysed transesterification. Experimental details, synthesis procedure and product confirmation is followed as per earlier communication on the synthesis of jatropha biodiesel [21]. The formation of methyl ester has been confirmed by Hydrogen-1 Nuclear Magnetic Resonance (^{1}H NMR) spectroscopy on a 500 MHz NMR spectrometer (Oxford, AS400, China). The fatty acid composition of the sample estimated using a gas chromatography technique (GC, CP-3800, Varian, Netherland) is reported elsewhere [22]. The prepared WCO biodiesel have been blended at two different ratios such as 10 and 15 % of diesel on a volume basis and labelled as B10 (10 % WCO biodiesel + 90 % high speed diesel) and B15 (15 % WCO biodiesel + 85 % high speed diesel). The blending is carried out using a mechanical stirrer for 40 min continuously to prepare a homogeneous mixture of fuel and biodiesel to achieve the best performance of the engine. After stirring the fuel

mixture is injected to fuel tank without any time lag. Prepared biodiesel and their blends are used to analyse the physico-chemical properties in order to carry out the further study on engine performance and emission characteristics. The physico-chemical properties of WCO methyl esters and their blends are examined according to ASTM and AOCS standard methods as reported in our earlier communication [21].

Engine Test Setup

The experimental set-up considered for testing of various blends is as shown in Fig. 1. This set up mainly consists of a single cylinder-4-stroke engine which is water cooled and runs at a constant speeds. This engine is naturally aspirated and has provision of direct injection (DI) of diesel in the hemispherical combustion chamber. The injection nozzle has three holes of 0.3 mm diameter with a spray angle of 120°. It is coupled with an eddy current dynamometer (SAJ Make, Model AG10) for measurement of torque at various loading conditions. The engine specification and associated measuring devices are listed in Table 1 [23].

Engine Instrumentation

The engine test rig is equipped with various measurement systems. These systems are mainly related to load application on the engine, temperature measurement, air flow rate measurement, fuel consumption measurement and exhaust analysis. This section deals with the specification of these sub-systems of the present experimental set-up. During the experimental study performance of the fuel has been analyzed at various engines loading conditions keeping the engine speed constant. In these experiments, the amount of loads on the engine has been varied by changing the input current of the eddy-current dynamometer. Thus the varied load is measured using the load cell of strain gauge type (0–50 kg). A burette glass is connected to the flow path of the fuel from a fuel tank to the fuel pump. This method enables the measurement of a volumetric fuel flow rate from a tank to the engine. In case of experiments with 100 % diesel, the tank is filled with diesel while for the experiments with biodiesel-diesel blend the tank is filled with the blend of interest. The air flow rate received by the present engine has been estimated from the pressure drop across the orifice meter mounted in the air path. A U-tube water manometer is attached for this measurement.

Coefficient of discharge of the orifice meter is 0.6. An exhaust gas analyzer 'Testo-350S/M/XL' is used for the quantitative assessment of the engine exhaust. This flue gas analyzer is helpful to quantify the presence of five gases

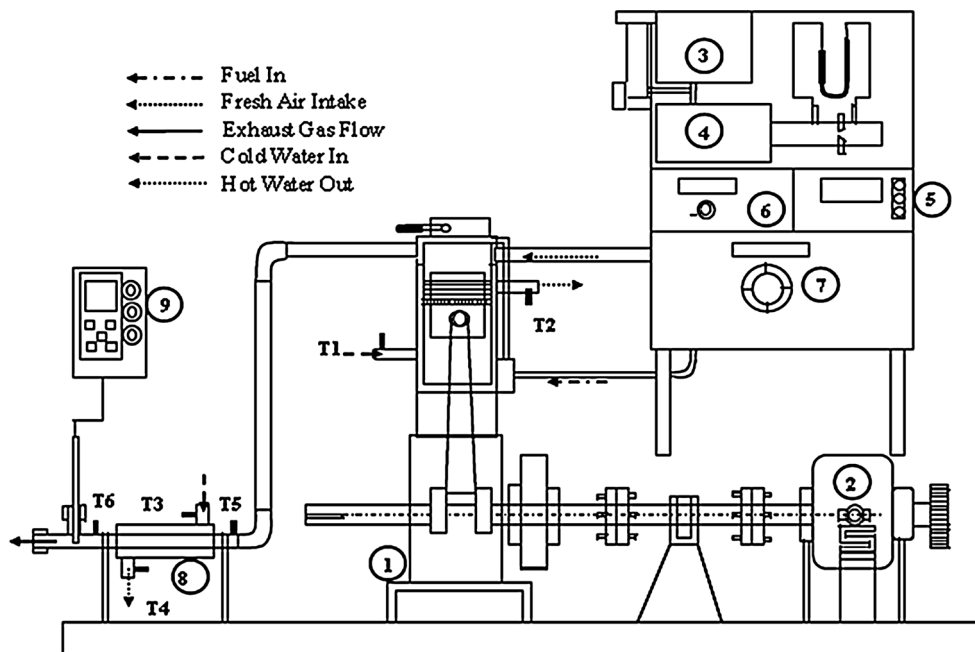**Table 1** Specification of diesel engine test bench, specification of diesel engine an associated systems

System specifications	
Make and model	Kirloskar, Model TV1
Engine type	Single-cylinder, 4-stroke, VCR DI diesel engine
Rated power	(diesel) 5.2 kW (7 BHP) @1500 rpm
Type of cooling	Water cooled
Bore × Stroke	87.5 × 110 mm
Swept volume	661 cc
Compression ratio	17.5:1
Speed	1500 rpm, constant
Injection timing	(diesel) 23°bTDC(27° to 10°bTDC)
Rotameters	Engine cooling 40–400 lph, calorimeter 10–100 lph

Table 2 Specifications of exhaust gas analyzer

| Emission	Range	Uncertainty (%)
O_2	0–25 vol%	±5
CO	0–10,000 ppm	±5
CO_2	0–50 vol%	±5
NO	0–3000 pm	±5
NO_2	0–500 ppm	±5
HC	0–40,000 ppm	±5
SO_2	0–5000 ppm	±5

viz. O_2, CO, CO_2, NO_X and HC generated as the products after combustion of diesel or diesel blends with WCOME. The manufactures specifications of the exhaust gas analyzer are as given in Table 2. A 'K' type thermocouple has also been used for measurement of exhaust gas temperature.

Results and Discussion

Product Confirmation by ^1H NMR spectroscopy

NMR spectroscopy has been recorded to observe the structural change and to monitor the transesterification reaction. In case of WCO ^1H NMR spectra multiplet, peaks are noticed in the region δ 4.12- 4.16 ppm and δ 4.27-4.31 ppm indicate the presence of methylene proton of –CH_2-CH-CH_2– glycerol group (Fig. 2). The completion of transesterificationreaction is confirmed by the presence of a characteristic peak of methoxy protons (–CH_3) as a singlet at δ 3.6 ppm. The change in ^1H NMR spectrums with WCO along with its methyl esters are shown in Fig. 2. The singlet at δ 3.6 ppm is indicative of WCO to methyl esters conversion. Therefore, from the ^1H NMR spectra of WCO and its methyl esters, it can be confirmed that WCO conversion into methyl esters is accomplished, and the

Fig. 2 ¹H-NMR spectrum of WCO (**a**) and methyl esters (**b**)
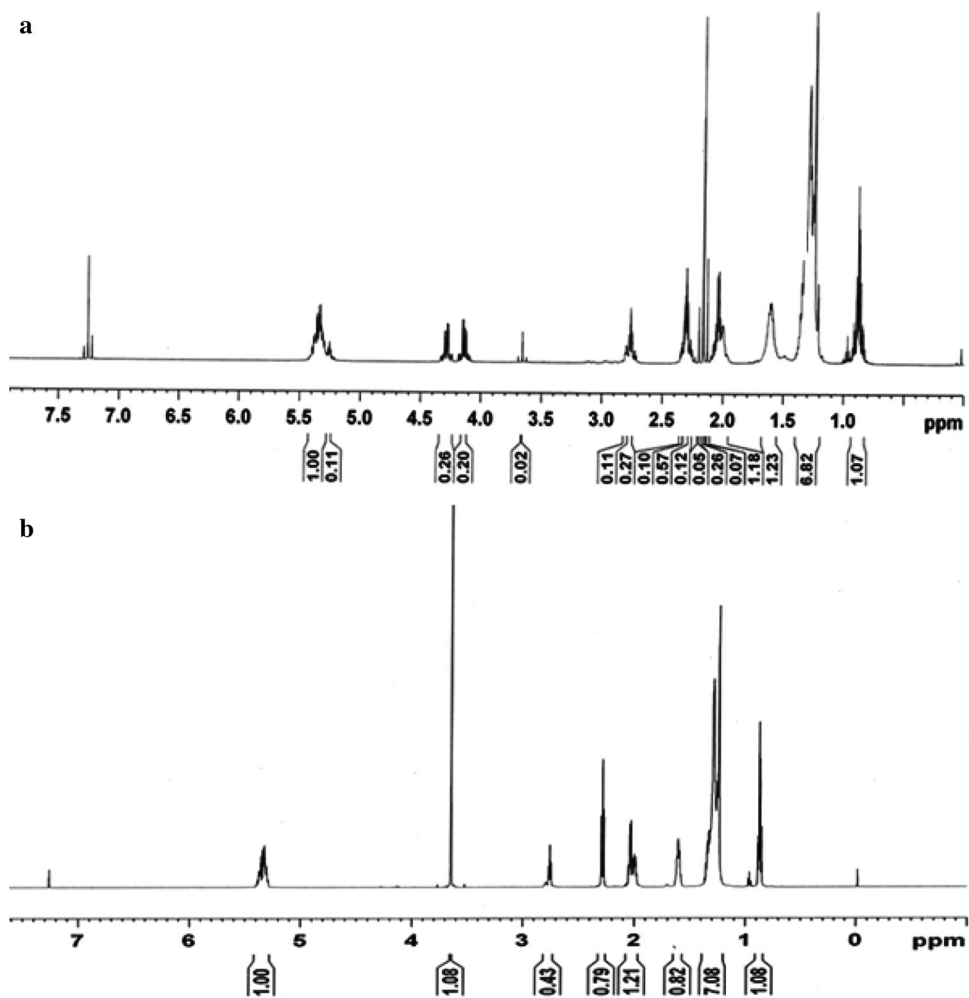
conversion is reported to be 96 % as per formula reported by Sharma et al. [24]

Physico-Chemical Characterization of WCOME and Their Blends

Physico-chemical properties of WCO, WCOME and their blend are evaluated as per ASTM standard methods and reported in Table 3. During the study kinematic viscosity and densities are found to be increased with an increase biodiesel ratio in the blends. These are highly significant properties, which influence the fuel atomization of the blends [25] and these properties are reduced significantly after transesterification.

The obtained values of biodiesel blends are in the satisfactory range of ASTM measures, along with WCO

Table 3 Physico-chemical characterization of WCOME and their blends

Properties	Unit	ASTM D6751*	Diesel	WCO	WCOME	10 % biodiesel	15 % biodiesel
Cloud point	°C	−3 to 12	8	14	7	9	11
Pour point	°C	−15 to 16	−3	1	−1	−3	−2
Flash point	°C	>52	66	305	180	82	86
Density	kg/m³	860–900	850.36	950	888.36	854.48	859.6
Calorific value	MJ/kg	>35	44.29	38.21	39.19	42.15	41.27
Kinematic viscosity (at 40 °C)	mm²/s	1.9-6	1.96	49.84	3.36	2.12	2.15

* Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels [28–30]

biodiesel density value. As reported earlier, considering the viscosity which is the serious problem in the utilization of plant seed oils for engine functioning is reduced considerably after transesterification. Similarly, flash point values decrease after transesterification and found to be in the range of diesel and WCO biodiesel. The higher flash point of blends and WCO biodiesel makes it safer for handling, storage and transportation [16]. Flash point temperature depends on viscosity; hence, reduced viscosity after transesterification may be one of the causes for a lower flash point of prepared methyl esters. However, boiling point of individual fatty acids also considered for a lower flash point. The reduced viscosity leads to improved atomization, fuel vaporization and combustion. Cold flow properties such as the cloud point found to be improved after transesterification, but there is no significant change in pour point value before and after transesterification. However, cold flow properties of prepared blends are in the permissible limit of ASTM standards. Higher heating value (HHV) is one of the crucial properties for evaluation of biodiesel, which allows the suitability of fuels as the substitute to conventional diesel fuels. HHV for WCO methyl esters found to be 39.19 MJ/Kg. The result shows that HHV of methyl esters is higher than the raw WCO (Table 3). From Table 3, it could be observed that, as blend percentage in diesel increases the calorific value decreases, due to the low calorific value of WCO biodiesel. Nevertheless, all the estimated blends properties are in the range of reported ASTM standards. Finally, it could be concluded that WCOME and their blend can act as potential candidates to use in a diesel engine.

Engine Performance Characteristics

Initial experiments are conducted for base line studies of the engine using diesel as the fuel, these experiments are followed by testing of different fuel blends. The fuels prepared for the testing purpose are B10 and B15. The same fuel injection pressure of 190 bars and crank position of 23° before the top dead centre (bTDC) has been considered for all blends. Tests are conducted at a rated speed of 1500 rpm while the load has been varied from 0 to 100 % in steps of 20 %. The engine jacket outlet water temperature at no-load condition is considered as the steady-state engine condition for all the blended fuels that are tested as one blends in a day basis, followed by flush off the blend fuel by running the engine on pure diesel for some time. Then the engine performance has been analyzed for a given fuel in terms of brake power (BP), brake thermal efficiency (BTE), brake specific fuel consumption (BSFC), exhaust gas temperature and emissions. Uncertainty involved during these estimations is given in Table 4.

Table 4 Uncertainty associated with computed parameters

Computed parameters	Uncertainty (%)
Brake power	±0.9
Brake thermal efficiency	±1.52
Brake specific fuel consumption	±1.14
Emissions	±5

Performance Characteristics

The variation of engine brake power with load for various blends is shown in Fig. 3. This Fig. 3 is necessarily portrays the self-validation of the experiments since the engine runs at a constant speed which in turn produces constant specific brake power at given load.

Thus the power being same for all the blends and diesel, the methodology of experimentation and associated measurements get validated. In present experimentation, governor attached on the camshaft of the engine regulates the flow of fuel to the engine as per load and maintains constant speed. As a result of this, the fuel flow rate supplied to the engine changes. This fact can be observed from Fig. 4, for the same load and power, more fuel is required in case of blends and this requirement also increases with an increase in the percentage of WCOME in diesel. During low load condition, it can be noticed that the brake specific fuel consumption (BSFC) for WCOME is 11 % higher whereas during the high load side, it is 8 % higher with respect to diesel fuel (B0) [26].

Overall increment of 10 % in BSFC with use of WCO biodiesel blends in comparison with base diesel tests [27]. Hence the brake specific fuel consumption is found to be
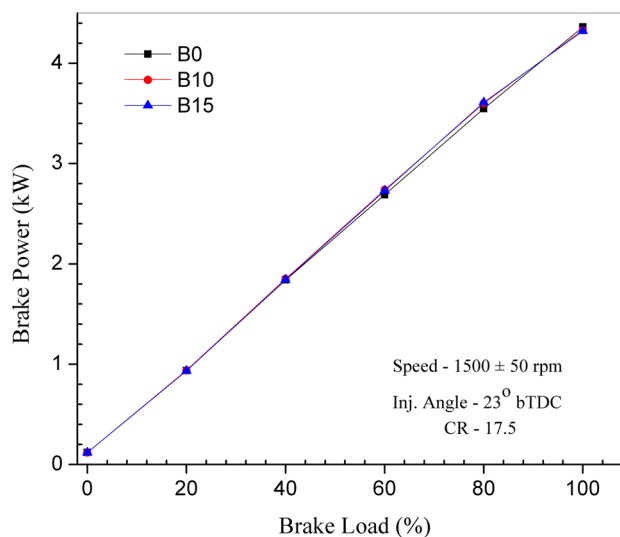

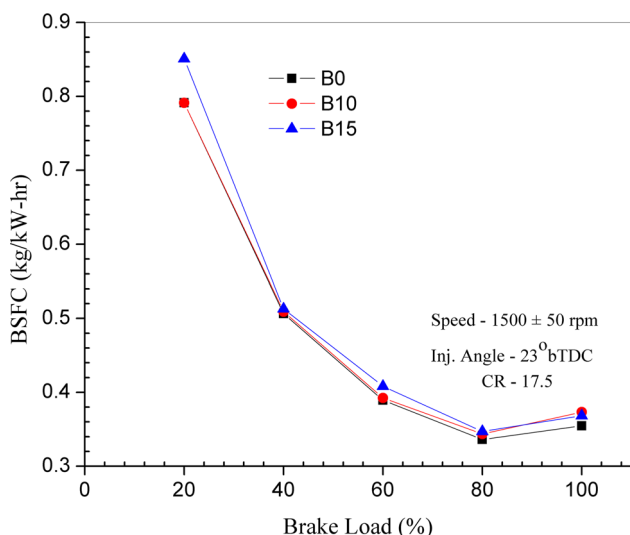**Fig. 3** Brake power variation with brake load

Fig. 4 Brake specific fuel consumption variation with the brake load

more for the same power in case of the blend. This indicates the higher fuel requirement for a given power, while considering WCOME as the blend with diesel. The major reason of this increment is the lower heating value of WCOME than that of diesel, which in turn reduces the heating value of the mixture. It is worth mentioning that the density and kinematic viscosity of WCOME are higher than those of diesel owing to which higher amount of blended fuel gets passed through the fuel injector [28].

Brake thermal efficiency (BTE) variation with load for pure diesel and WCO biodiesel blendedfuel is plotted in Fig. 5. The BTE is found to be increasing with an increase in load on the engine till a critical vlaue ($\sim 80\%$) beyond which BTE decreases for all fuels with the further increase in load [29].
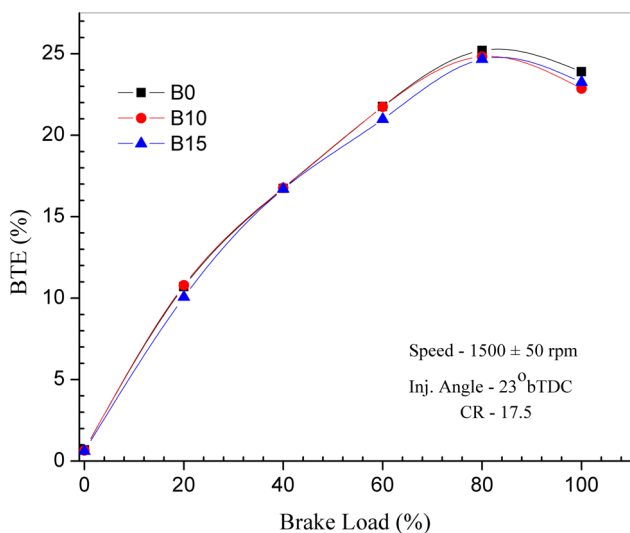
This critical load value is found to be independent of the WCOME percentage in the diesel. Moreover, for a given load, BTE decreases with an increase in the blend percentage. The higher fuel economy at lower blended rates, as noticed in Fig. 4 justify the decrement in BTE with an increase in the amount of blend in fuel. Thus the lower heating value along with higher specific gravity and viscosity of WCOME affects air–fuel ratio and lowers the brake thermal efficiency with respect to diesel [30].

The exhaust gas temperature (EGT) is the form of loss of heat produced by combustion of fuel and air mixture in a cylinder. The EGT isan important factor for thermodynamic analysis of the engine used with different fuels. The variation of EGT obtained from the present set of experiments is plotted in Fig. 6. Although less variation in EGT is seen for different blends at low and high load sides, experiements with pure diesel show higher EGT at intermediate loading conditions. The lower EGT of biodiesels for the same brake power and at the cost of higher BSFC is probably due to the poor atomization rate of fuel blends in the combustion chamber due to higher viscosity, specific gravity and poor volatility [31, 32]. Apart from this, the longer ignition delay of diesel results in higher exhaust gas temperature [33].

Emission Characteristics

The emissions of carbon monoxide (CO) with a varying load is described in the Fig. 7. The CO emission is increases with an increase in load on the engine for all fuels. Initial increment in CO emission up to 40 % load is negligible. However, it increases at a higher rate with a further increase in the load. The CO emission is found always higher for diesel fuel, which is around 11.4 % at
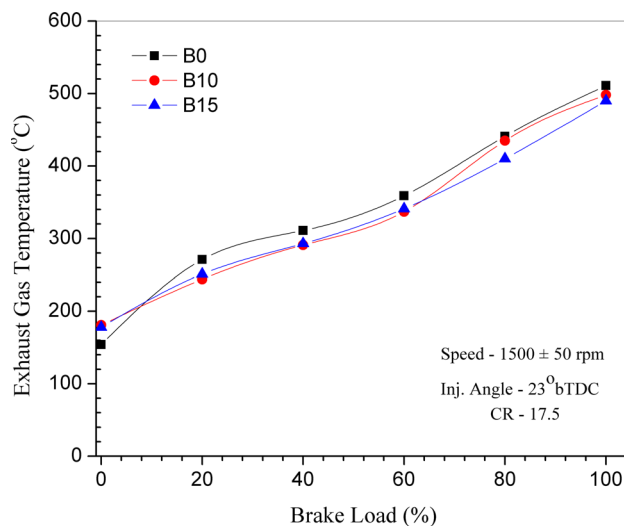

Fig. 5 Brake thermal efficiency variation with the brake load

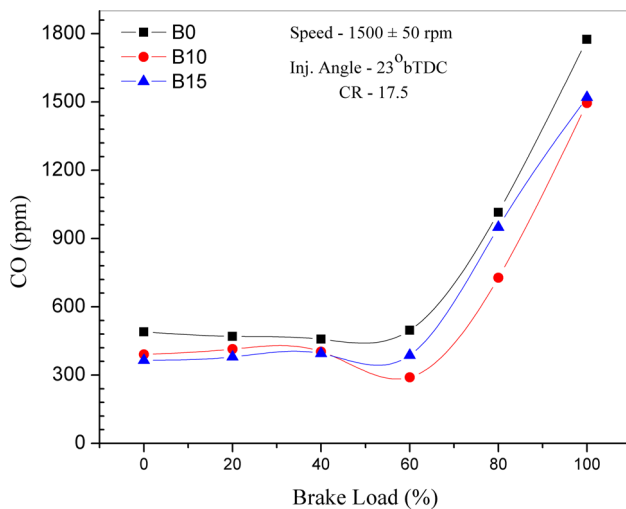**Fig. 6** Exhaust gas temperature variation with the brake load

Fig. 7 Variation of CO in the exhaust with the brake load

lower load and 31.67 % at high load conditions in comparison with B15 [32].

The WCO biodiesel–diesels blend and conventional diesel fuel show increase in NOx emission due to increase in load as shown in Fig. 8.This NOx emission is found to be 22.69 and 27.68 % lower in B15 blend on lower and higher load respectively in comparison with base diesel tests. The NOx formation in the diesel engine is strongly dependent on the fuel distribution and its evolution with time [34]. Thus the altered fuel distribution for blended fuels, due to change in physical properties of the fuel alters the percentage of NOx in the exhaust [35].

Apart from this, expected a higher value of the peak cylinder pressure and peak combustion temperature in case of diesel fuel are responsible for higher NOx in exhaust for
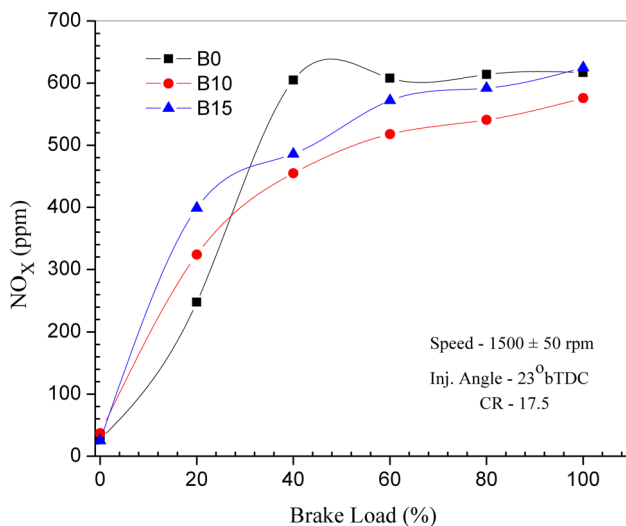
diesel fuel [36, 37]. They also reported that fuel cetane number and aromatic taste increase NOx in the exhaust.

The effect of B0, B10, B15 fuel blends on CO_2 emission is summarized in Fig. 9. CO_2 emission increases with an increase in load for any fuel under consideration. Along withthis, it is seen to be lower in WCOME biodiesel-diesel blend with respect to the diesel. In particular, it is 15.77 and 17.6 % lower for B15 at 20 and 80 % loads with respect to diesel emission. These results are in good agreement with the observations of Behcet [38]. Thus the oxygenated biofuel substantially reduces the CO_2 emission, mainly at low load conditions [39]. Therefore, this Fig. 9 reconforms the fact that the reduced carbon content in blends is responsible for lower CO_2 emission [40].

The hydrocarbon (HC) emission which is mainly the left unburnt fuel varies with the engine loading as shown in Fig. 10. The HC emission initially decreaes with an increase in the load, attains a minimum and then increases with the further increase in engine load for all the fuels under consideration. Consistently it has been observed the HC emission is higher in case of diesel than any blends considered herein. In particular, it is 8.5 and 20 % lower for B15 WCO biodiesel-diesel blend for 40 and 80 % loads with respect to the diesel. Two major reasons can be given for the lowered HC emission in case of blended fuels. Among which one is the expected lower ignition delay of blended fuels than the diesel improcess cetane number, which in turn avoids the accumulation of fuel in the combustion chamber [41–43]. Secondly, biodiesel blends to have higher oxygen availability in the fuel itself so even if the mixture is reached, the HC produced is comparatively less than diesel fuel. As a result of these, exhaust for blends found with lesser HC percentage [44, 45].
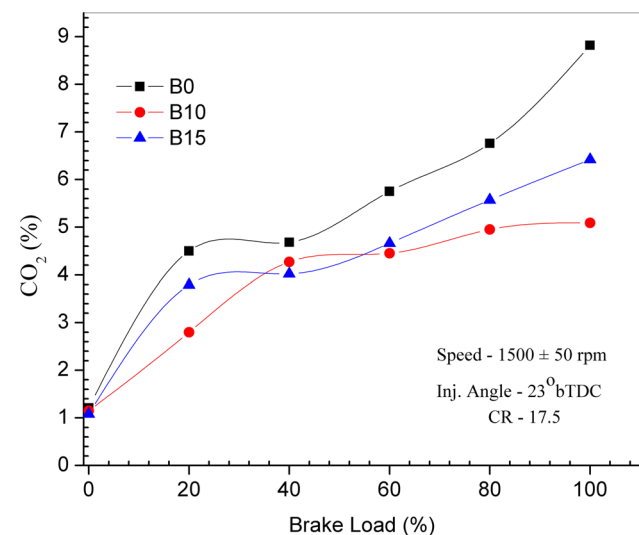

Fig. 8 Variation of NOx in the exhaust with the brake load

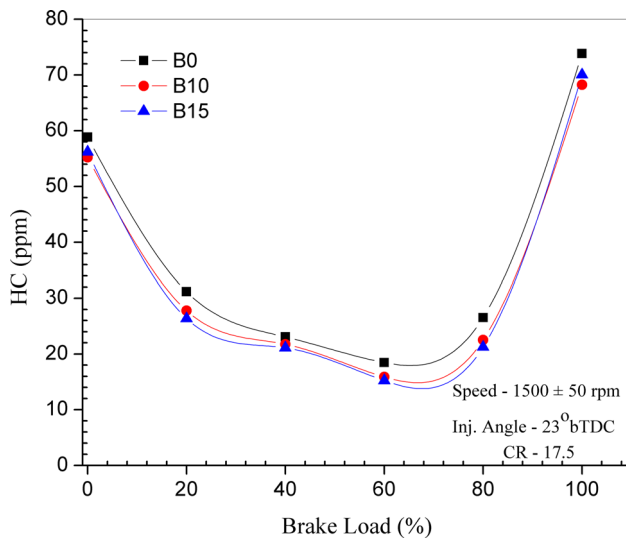**Fig. 9** Variation of CO_2 in the exhaust with the brake load

Fig. 10 Variation of HC in the exhaust with the brake load

Conclusions

An experimental investigation of WCOME blends with conventional diesel is carried out to explore the diesel engine performance and emissions. Results of the study show 2.70 % overall decrease in maximum efficiency and 9.1 % increase in the brake specific fuel consumption for blended fuel B15 compared to diesel fuel. The reduce exhaust gas emission (i.e. CO, HC and CO_2) as well as a decrease exhausts gas temperature attributes to the reduce ignition delay during combustion. Prepared blends are found more effective in lowering all the constituents of emission except NOx emission. The increase in the NOx emissions is 0.7 % especially at higher load. Thus the blending of bio-diesel with the conventional diesel is noted to be slightly less economical in terms of fuel consumption, but it is highly desirable to provide cleaner exhaust. Further, techniques such as exhaust gas recirculation can be considered to reduce the NOx emissions.

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