Indian Journal of Chemical Technology
Vol. 24, July 2017 pp. 393-399

An emission analysis on the role of TiO_2 additives in kusum oil methyl esters on working characteristics of CI engine

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Received 10 February 2015; accepted 8 February 2017

The role of emission characteristics of a diesel engine has been investigated when titanium dioxide (TiO_2) nano additive blended with Kusum oil methyl ester (KOME) are used as a fuel. Biodiesels produced from kusum oil by transesterification process. The additive ((TiO_2) is added to B20 at a dosage of 50 ppm and 100 ppm. The kusum oilmethylester (KOME) is mixed with TiO_2 nanoparticles with the aid of an ultrasonicator. The fuel properties of B20, (80% Diesel + 20% KOME), B20TiO_2 50 (80% Diesel+20% KOME+50ppm TiO_2) and B20TiO_2 100 (80% Diesel+20% KOME+100ppm TiO_2) have been studied and compared according to ASTM standard test methods for biodiesel. Tests are performed at full load CI (Compression Ignition) engine operation with a constant speed of 1500 rpm. The results show that the compression ignition engine works well and the power outputs are steady running with the selected biodiesels blends at different loads. The acquired data are studied for various parameters, such as exhaust emission of Hydro Carbon (HC), Carbon monoxide (CO), Carbon dioxide (CO_2), Oxides of nitrogen gases (NOx) and smoke opacity.

Keywords: Kusum oil methyl ester, Ultrasonicator, Titanium dioxide nanoparticles, Emission

Biodiesel can be derived from vegetable oils with edible and non-edible grade, waste vegetable oils as well as from animal fats which offer many novel advantages that make biodiesel in general an attractive proposition for unaltered CI engines. Vegetable oil based ester fuels can be derived from a number of edible, non-edible grade oil sources such as peanut, sunflower, palm, soybean, sesame, rapeseed/canola, mustard, sunflower, linseed, coconut, jatropha curcas, karanjia, Pongamia pinnata, mahua, neem, pine seeds, tung seeds, nagchampa, kusum etc.[1]. In the present study, the kusum seed oil, a non-edible type vegetable oil is chosen as a potential alternative for producing biodiesel and use as fuel in compression ignition engines. In India, Kusum is one of the forest based tree borne non edible oil. The botanical name of Kusum is Schleichera oleosa is widely found in the sub Himalayan region, Chattisgarh, throughout centra and southern India. The estimated availability of kusum seed is about 25,000 oil potential per tonnes per annum. In the past kusum seed oil was exported from India to Germany. Kusum seed kernels (0.45 lacks of tones of seed) contain 40.3% of yellowish brown colored oil. The one or two almost round seeds some 1.5 cm in diameter and weighing between 0.5 and 1.0 g. The oil content is 51-62% but the yields are 25, 27% in village ghanis and about 36% oil in expellers. It contains only 3.6 to 3.9% of glycerin while normal vegetable oil contains 9-10% glycerine. The viscosity of kusum oil was found to be higher than that of diesel fuel. The high viscosity of kusum oil may be due to its larger molecular weight compared to diesel. The flash point of kusum oil was higher than diesel and hence it is safer to store. It is seen that the kinematic viscosity of kusum oil is 40 CSt at 40°C and after blending decreases gradually closer to that of diesel[2].

Venkatesan *et al.* determined a considerable enhancement in the brake thermal efficiency, improved BSFC and decreased concentration of HC, NO_x and smoke in the exhaust emitted from the diesel engine, without changing the engine system at 0, 25, 50, 75 and 100% load condition, when using aqueous CeO_2 at the rate of 50cc per liter dispersed into diesel and diesel–biodiesel. They also found that the higher catalytic activity of the CeO_2 nanomaterials improved the fuel combustion[3]. Sajeevan *et al*. investigated the effect of CeO_2 nanoparticles as additive in standard diesel on the physicochemical properties of the standard diesel as well as the engine performance and emissions. The work also involved the synthesis of CeO_2 nanoparticles by precipitation method which is a chemical method. The fuel properties tested include flash point, fire points and viscosity. The single cylinder water-cooled direct injection diesel engine was used for conducting the engine performance tests. The engine performance and emission characteristics were analyzed. The experimental investigations were carried out by varying the dosage levels of nanoparticles in the standard diesel from 5 to 35 ppm. The stability study of the nanofluid was also carried out with the addition of surfactants in the standard diesel. They concluded that the flash point and fire point were increased while increasing the dosage level of CeO_2 nanoparticles in the standard diesel, even though the kinematic viscosity was increased with the CeO_2 nanoparticles addition in the standard diesel, it was found to be decreasing with the addition of surfactant DDSA, the results of the load test showed that the efficiency was increased up to 5% and a reduction of HC and NO_x emissions were achieved by 45 and 30%, respectively, especially at higher load conditions, the reduction in the emissions were proportional to the dosage level of CeO_2 nanoparticles in the standard diesel and the optimum dosage level of CeO_2 nanoparticles was observed as 35 ppm[4].

The application of nano-additive in liquid fuel is an interesting concept and its full potential is yet to be explored. In this context, Al_2O_3 nanoparticles were incorporated into the diesel fuel to investigate performance, emission and combustion characteristics of a four stroke single cylinder diesel engine. The Al_2O_3 nanoparticles (25, 50 and 100 ppm) were doped into the neat diesel using an ultrasonicator and the prepared fuel samples were subjected to stability tests. Subsequently, the experiments were conducted in a diesel engine at a constant speed of 1500 rpm using Al_2O_3 nanoparticles blended diesel fuels and the results were compared with those of neat diesel. The experimental outcome revealed a substantial enhancement in the brake thermal efficiency and a marginal reduction in the emissions of harmful pollutants (NOx, CO and smoke) for the nanoparticles blended diesel fuels when compared to the neat diesel. Even though, the Al_2O_3 nanoparticles blended diesel fuels imparts better engine performance, efforts are also underway to trap the possible nanoparticles from the exhaust in order to protect the global environment[5].

Experimental measurements and analysis of ZnO nanoparticle additives combustion in diesel fuel were carried out at different dosing levels of the nanoparticle additives. The ASTM standard tests for the fuel property measurements were reported in this paper for bio diesel modified by the addition of ZnO nanoparticles. The fuel characterization data showed some similarities and differences between B20 and B20 with nano additives. The ZnO nano additive blends were found slight improvements in calorific value and kinematic viscosity compared to B20. It is studied that the maximum cylinder pressure is high for ZnO nano additive fuels which speeds up the early initiation of combustion and the ignition delay decreases. The decrease in BSFC can be due to the positive effects of nanoparticles on physical properties of fuel and also reduction of the ignition delay time. The combustion characteristics improved by the lighter surface – area – to- volume ratio of nano particles which is allowed more amount of fuel to react with air. It leads to enhancing in BTE. By and large, it is observed that the minimum CO and HC emission was measured with the use of ZnO blend fuels compared to B20, while the maximum NOx emission was recorded with the use of ZnO blended fuels[6].

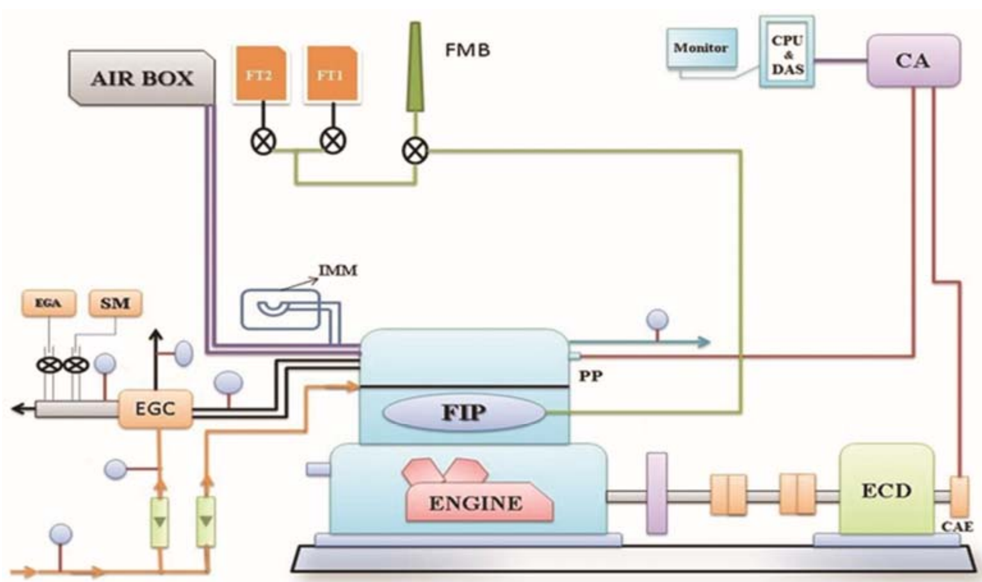
The performance and emission characteristics of B20, D80B20ZnO50 and D80B20ZnO100 pomolion stearin wax biodiesel blends are investigated in the single cylinder diesel engine. ASTM standard tests for the blended fuel property measurements were described in the addition of zinc oxide nanoparticles. The zinc oxide nano additive blends showed an improvement in calorific value. The addition of nanoparticles for blends has been reduced the brake specific fuel consumption, while the brake thermal efficiency increases with the increasing in all engine loads. The CO, HC and smoke opacity are appreciably reduced with the addition of zinc oxide nanoparticles. The NOx emissions of all blended fuels as no significant differences were observed[7]. The effect of ZnO nanoparticles with GSOME was considered as a possible alternative fuel for compression ignition engines. The GSO was transesterified under optimal reaction condition and obtained the GSOME. The important properties of ZnO nanoparticles with GSOME have been analysed. The ZnO nano particle blends showed an improvement in calorific value compared to D80B20. For each engine load, the test results indicated that there is an increasing BTE and decreasing BSFC with increasing the proportion of ZnO nanoparticle in the blended fuel. The EGT of ZnO nanoparticle in the blended fuels is marginally higher compared to D80B20. It is observed that there is an increase in NOx and CO_2 emissions for the ZnO nanoparticle blends. But CO, HC and Smoke emissions are lower for ZnO nanoparticles blended fuels[8]. The effects of Co_3O_4 nano additive with GSO Methyl Ester with different blends on performance and exhaust emissions of a direct injection diesel engine were experimentally investigated. The calorific value and flash point increase with the dosing level of Co_3O_4 nanoparticles in blends. The Exhaust gas temperature for Co_3O_4 nanoparticles blends was lower than that of D80B20. Considerable improvement in brake thermal efficiency was observed with Co_3O_4 added blends compared to D80B20. But, the brake specific Fuel consumption for Co_3O_4 nanoparticles present in the blends is lower than the D80B20 at full load operating condition. Compared with D80B20, emissions like HC and CO were reduced in the case of Co_3O_4 added blends. Smoke opacity and NOx emission were found to be less for Co_3O_4 added blends[9].

There are few reports based on the biodiesel blended with nanoparticles additive, however, there is a vacuum in the research pertaining to the use of the most common, low-cost and eco-friendly TiO_2 nanoparticles as additive to prepare blended biodiesel fuel. Moreover, there are very few literatures available on the usage of TiO_2 blended biodiesel. Based on these facts and also, by considering the same as a significant research gap in the field of biodiesel, the present investigation has been focused on the preparation of different biodiesel blends with an aid of TiO_2 additives, in view of their long-term applications in single cylinder compression ignition engine towards beneficial support to all community.

Experimental Section

Test engine

Single cylinder four stroke diesel engine (Kirloskar) coupled with an eddy current dynamometer is one of the commonly used engines for small, medium and high scale commercial purposes. It can withstand the peak pressure because of its enormous compression ratio. An experimental setup was advanced to conduct experimentations on



ECD (Eddy Current Dynamometer)	FT1 & FT2 (Fuel tanks)
DAS (Data Acquisition System)	SM (Smoke Meter)
PP (Pressure Pickup Transducer)	IMM (Inlet Manifold Manometer)
CA (Charge Amplifier CPU)	EGA (Exhaust Gas Analyzer)
CAE (Crank Angle Encoder)	EGC (Exhaust Gas Calorimeter)
FMB (Fuel Measuring Burette)	FIP (Fuel Injection Pump)

Fig. 1 — Experimental setup

the selected compression ignition engine with different fuel types to estimate performance and emission parameters at different operational conditions. The various components of experimental setup are described below. Figure 1 shows the line diagram photograph of the experimental setup. The test engine used was a four stroke, single cylinder, direct injection, water cooled and naturally aspirated CI engine. It had a bore of 87.5 mm and stroke of 110 mm. The maximum power delivered by the engine was about 5.2 KW at a constant speed of 1500 rpm and the compression ratio of 16.5:1. The suggested injection pressure and injection timing were 210 bar and 23°C ABTDC, respectively.

Smoke meter

The smoke meter used in this study was AVL 437 C smoke meter. It was used to measure the smoke opacity of the test engine. The opacity is the destruction of light between light source and receiver. The exhaust gas was fed into a chamber with non-reflective internal surfaces. The active length of the light absorption track was calculated depending on the category of the light source and the photocell working in the instrument. The actual length was 0.430 ± 0.0005 m. Light scatter on the photocell from diffused or reflections light inside the chamber was decreased to a minimum by the use of matt black light traps. The light source used was a luminous bulb with a color temperature between 2800K and 3250K. The reaction time of the electrical circuit was identified as between 0.9 and 1.1 s within which the indicator reached 92% of the full scale when a totally opaque plate was located in front of the photocell. The specifications of the smoke meter are given in Table 1.

Exhaust gas analyzer

Combustion of air fuel mixture inside the engine cylinder is one of the important processes that control the engine power, performance and emission. The exhaust emissions from the engine contain huge amount of contaminants, which usually combined with smoke and these pollutants can be measured by using five gas emission analyzer. The five gas emission analyzer was used to measure the CO, HC, O_2, CO_2 and NO_X emissions. The HC, CO, and CO_2 emissions were found out based on the non-dispersive infrared measurement method while their O_2 and NO_X emission were obtained based on the electrochemical measurement method equipped with the analyzer. He measurement resolution for different gases were HC = 1 ppm, CO = 0.01%, CO_2 = 0.01%, O_2 = 0.01% and NO_X = 1 ppm. When the probe was inserted into the exhaust pipe of the engine, the exhaust gas passed through a metal mesh screen to filter the soot and dust particles after which it was allowed to pass through a fine fiber element which filtered the entire gas for any foreign particles and also cold traps were provided to prevent moisture from entering the exhaust gas analyzer. Then, the clean and cool sample gas entered the direct sensor measurement through filter arrangement and the readings were displayed on the screen and saved. The emission measurements were carried out on dry basis. The specifications of the exhaust gas analyzer are given in Table 2.

Table 1 — Technical specifications of smoke meter

Working temperature range	: 4°-50°C
Ambient pollution	: 3% max.
Working humidity range	: 10%-98%
Collimation	: 4°
Source light	: Green led 570 nm
Detector	: Gallium arsenide
Response time	: 1.5 m sec
Physical path length	: 175 mm
Resolution	: 0.01%
Optical path length	: 367 mm
Inner Ø of sample cell	: 25 mm
Opacity accuracy	: ± 3% relative
Storage temperature	: −33°C - +58°C

Result and discussion

FTIR studies of biodiesel

The infrared spectrum of KOME showed the presence of pronounced functional groups, which indicated the presence of alkanes and poly-aromatic groups with an absence of phosphorus and sulfur. The typical FT-IR spectrum of the transesterified Kusum oil showed that it contained significant amount of esters. The comparative frequency ranges of the spectra, their corresponding functional groups and indicated compounds have been presented in Fig. 2.

Different bonds were present in biodiesel (C-C, C=C, C-O, C=O, O -H, N -H etc.) have different vibrational frequencies. The presence of these bonds

Table 2 — Technical specifications of the exhaust gas analyzer

Parameter	Resolution	Accuracy	Range
CO	1 ppm	± 20ppm (for < 400 ppm CO)	0 - 10000ppm
HC	0.3%	± 10 ppm (for < 100 ppm HC)	0 - 5000 ppm
O_2	0.1%	−0.1% + 0.2%	0-25%
CO_2	0.1%	± 0.3%	0 - Fuel value
NO	1 ppm	± 5 ppm (for < 100 ppm NO)	0 - 5000 ppm
SO_2	1 ppm	± 5% (for >100 ppm SO_2)	0 - 5000 ppm
NO_2	1 ppm	± 5 ppm (for < 100 ppm NO_2)	0 - 1000 ppm
Pressure	0.01 mbar	±0.5% Full scale	0 – 150 mbar

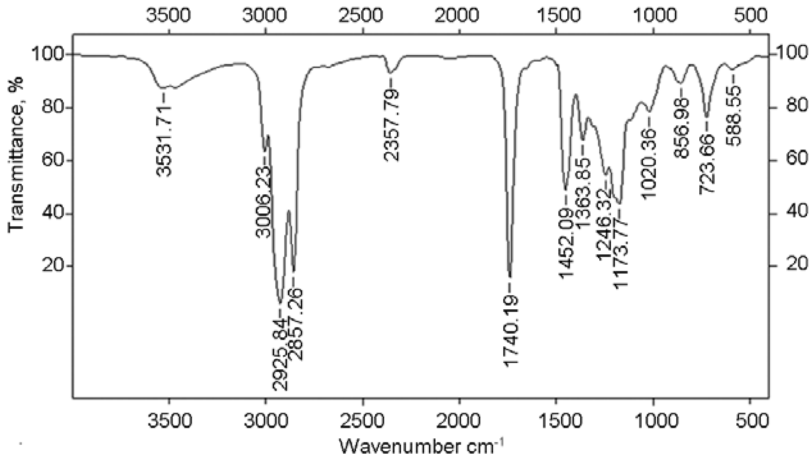


Fig. 2 — FTIR studies of KOME

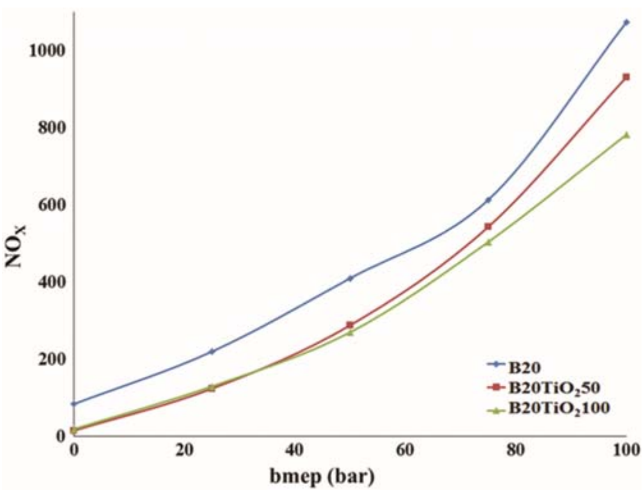


Fig. 3 — Variation of NOx with bmep

in biodiesel could be detected by identifying characteristic frequencies as absorption bands in the infrared spectrum. Functional group vibrations were made for most of the dominant peaks. The carbonyl band in FTIR was sensitive to substituent effects and to the structure of the molecule. From the spectrum, it was observed that the peak of C=O vibration band (in the range 1750–1735 cm^{-1}) of methoxy carbonyl group changed from 1743 cm^{-1} in oil to 1740 cm^{-1} in biodiesel. Biodiesel could be elucidated from the absorption peak at 1743 cm^{-1} corresponding to C=O stretching and hence the resultant product was confirmed as biodiesel. The ester carboxyl band at 1740 cm^{-1} indicates the formation of compounds containing other C=O groups. The broad band appeared at 3400 $cm^{-1}$was attributable to the –N-H-stretch. Hydroperoxides formed during oxidative process would have given rise to characteristic –O-O-H stretching vibration at approximately 3531 cm^{-1}. The peak at 3006 cm^{-1} was attributed to –HC = CH– stretching of methyl ester.

The vibrational peak appeared at 2925 cm^{-1} of the biodiesel was corresponded to asymmetric CH_3 stretching of weaker band. The asymmetric CH_3 deformation near 1455 cm^{-1} and the symmetric CH_3 deformation near 1375 cm^{-1} were observed. The vibrational peak at 3002 cm^{-1} was assigned to O -CH_2 asymmetric stretching of methyl ester. C-O-C stretching at 874 cm^{-1} and isophthaletes at 730 cm^{-1} were present in the biodiesel. Actually esters were characterized by the strong absorption due to C=O stretching frequency near 1740 cm^{-1} and by the strong absorption involving the stretching of C- O near 1240 cm^{-1}.

NO_x emissions

The comparison of NOx emissions for the B20, $B20TiO_2 50$ and $B20TiO_2 100$ fuels is depicted in Fig. 3. The TiO_2blended fuels produced lower NOx emissions due to the substantial heat sink effect during the combustion in the engine. Due to the localized lower temperature in the combustion chamber, there could be a subsequent dilution of gas species[10] associated with the TiO_2 blended fuels leading to reduction in the NOx emissions. This could be also due to better homogenization of reactant mixture, improved combustion and reduced exhaust gas temperature. The TiO_2 blended fuels could have absorbed heat rapidly, thereby decreasing the burning gas temperature inside the combustion chamber, and thus could have restrained the NOx emissions when compared to that of B20 fuel.

HC emissions

The variation of HC emission for the B20, $B20TiO_2 50$ and $B20TiO_2 100$ fuels is presented in

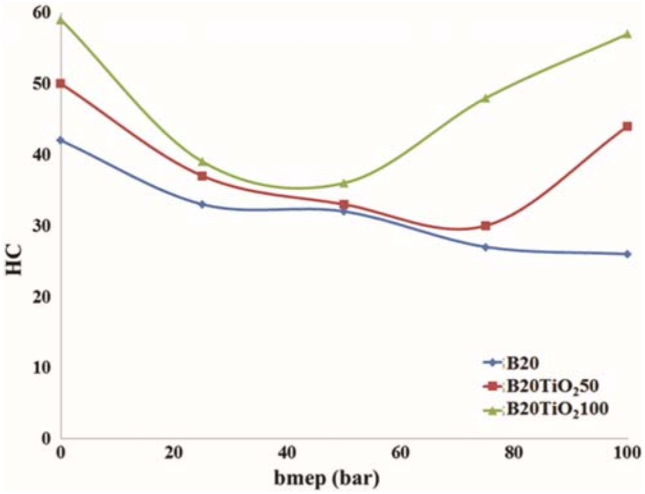


Fig. 4 — Variation of HC with bmep

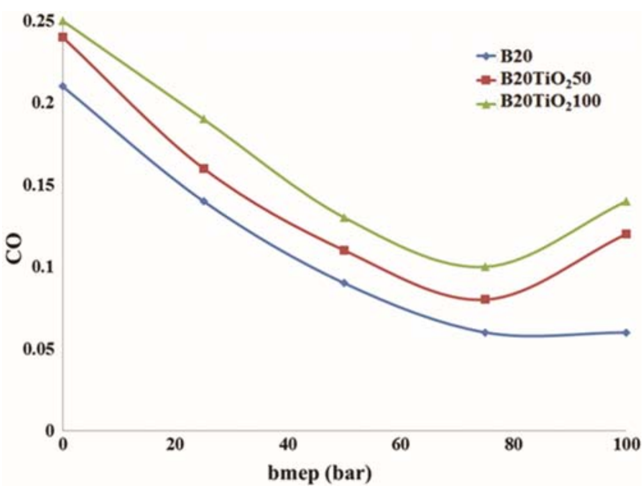


Fig. 5 — Variation of CO with bmep

Fig. 4. It was inferred from the figure that the HC emissions for the TiO_2 blended fuels were high compared tothat of TiO_2 blended fuels. The B20 blended fuel produced a marginal reduction in the HC emissions when compared to that of`TiO_2 blended fuels. This could be due to the intensive secondary atomization and significant fuel distribution in the presence of KOME in the combustion chamber and thereby causing the hydrocarbon oxidation. Due to those effects, there was a marginal reduction of HC emissions for the KOMEfuels when compared to that of TiO_2 blended fuels.

CO emissions

It is observed from Fig. 5 that the TiO_2 blended fuelsproduced higher CO emissions when compared to that of B20 blended emulsion fuel. At the lower loads, the fuel supplied was less i.e., the mixture

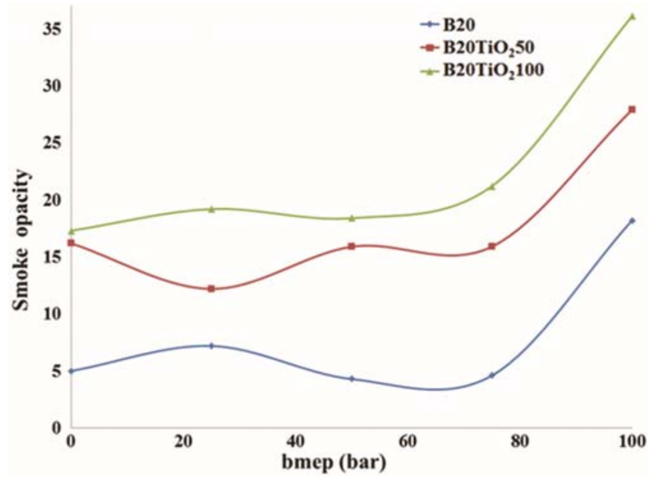


Fig. 6 — Variation of Smoke opacity with bmep

remains lean which produced lesser heat resulting in lower flame temperature, and hence there was no significant difference in the CO emissions among the tested fuels[11]. Whereas at the higher loads, the longer ignition delay problem associated with the TiO_2 blended fuels induced poor fuel–air mixing in the engine cylinder leading to high CO emissions compared to that of B20 fuel. On the other hand, the B20 blended emulsion fuel showed accelerated combustion due to the shortened ignition delay characteristics. Due to the shorten ignition delay effect associated with the B20 blended emulsion fuel, the degree of fuel–air mixing and uniform burning could have improved in the presence of potential KOME leading to complete combustion. Hence, there was an appreciable reduction of CO emissions for the B20 blended emulsion fuel when compared to that of TiO_2 blended fuels.

Smoke opacity

The variation in smoke opacity for the B20, B20$TiO_2$50 and B20$TiO_2$100 fuels is illustrated in Fig. 6. It is observed from the figure that there is a significant reduction in the smoke emissions for the B20 emulsion fuel when compared to that of TiO_2 blended fuels. This was due to the rapid evaporation of fuel in the fuel-rich regions, increased spray momentum and enhancement in the OH radicals[12] which were very effective in the oxidation of soot precursors. On the other hand, the addition of KOME to the fuel has shown a pronounced effect on further reduction of smoke emissions[13,14] compared to that of TiO_2 blended fuels. This was likely due to the occurrence of reduced soot formation and improved reactant mixture due to the rapid secondary atomization effects[15] in the presence of KOME.

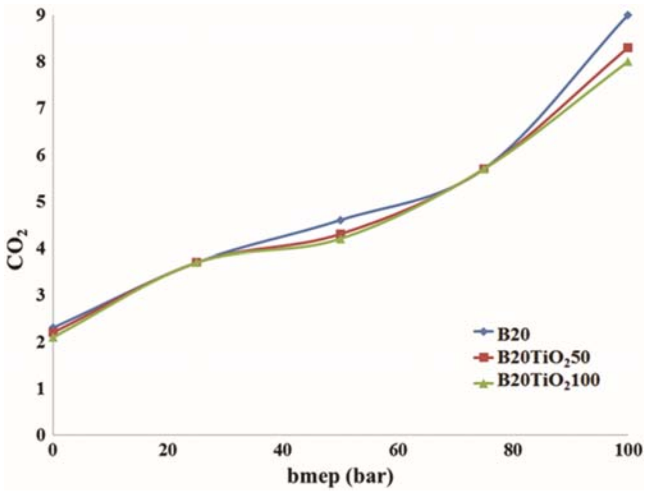


Fig. 7 — Variation of CO_2 with bmep

CO_2 emission

Figure 7 depicts the CO_2 emission of various fuels used. The CO_2 emission increased with increase in load for all blends. TiO_2 blended fuels emits less amount of CO_2 in comparison with B20. This is due to the fact that TiO_2 blended fuels are a low carbon fuel and has a lower elemental carbon to hydrogen ratio than B20. Using B20 blends, an increase in CO_2 emission was noted, which is due to the incomplete combustion. The CO_2 released from the TiO_2 blended fuels during combustion had been protected from the greenhouse effect.

Conclusion

The studies on performance and emission characteristics of a different KOME blended with TiO_2 nanoadditives is performed by a four stroke single cylinder, naturally aspirated, water cooled, direct injection diesel engine under different operating condition. The emission characteristics of a direct injection diesel engine using neat B20, B20TiO$_2$50 and B20TiO$_2$100 fuels are investigated. Based on the experimental investigations, the following conclusions are drawn. The level of harmful pollutants in the exhaust gases (NOx and CO_2) was radically reduced when compared to that of B20. Compared with B20, emissions like HC and CO were increased in the case of TiO_2 added blends. The smoke opacity emission is also found to be high for TiO_2 added blends. However, critical investigations are also in progress to run the diesel engine in order to safeguard the global environment.

References

1 Anpu M V, Ajaya Varma K & Baiju B, *Tech Congress*, (2011) 28.
2 Rathod N P & Lawanka S M, *Inter J Emerg Tech Adv Eng*, 3 (2013) 1.
3 Venkatesan S P & Kadiresh P N, *Inter J Ambient Energy*, 5 (2014) 1.
4 Sajeevan A C & Sajith V, *J Eng*, ID 589382, pp. 1-9.
5 Sadhik Basha J, *SAE Technical Paper* (2014) 1.
6 Karthikeyan S, Elango A & Prathima A, *Indian J Eng Mater Sci*, 21 (2014) 83.
7 Karthikeyan S, Elango A & Prathima A, *J Sci Indus Res*, 73 (2014) 187.
8 Karthikeyan S, Elango A & Prathima A, *Indian J Geo-Marine Sci*, 43 (2014) 564.
9 Karthikeyan S, Elango A & Prathima & Raja R, *Res J Chem Env*, 85 (2014) 14.
10 Jamil G, Honnery D & Al-Khaleefi K, *Appl Therm Eng*, 26 (2006) 12.
11 Sethi V P &Salariya K S, *J Inst Eng*, 85 (2004) 1.
12 Subramanian K A & Ramesh A, Use of diethyl ether along with water–diesel emulsion in a DI diesel Engine, *SAE*, 2002-01-2720.
13 Moy D, Niu C & Tennent Het, Carbon nanotubes in fuels, US Patent 2002-6419717, 2002.
14 Sadhik Basha J & Anand R B, *J Power Energy*, 225 (2011) 279.
15 Kadota T &Yamasaki H, *Prog Energy Combust Sci*, 28 (2002) 385.