Effect of Nitrate-based Cetane Improver on Ternary Higher Alcohol Biodiesel Blends and Diesel Engine Exhaust Emissions

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Abstract: Biofuels such as biodiesel and bioalcohols are promising alternative sources of renewable energy. However, the lower cetane number of diesel-biodiesel-alcohol blends is a critical issue, resulting in higher noxious engine pollutants. The objective of this study is to investigate the effects of blending diesel with 10 vol% of palm biodiesel, 10 vol% of pentanol (long-chain alcohol), and 1 vol% of ethyl hexyl nitrate (EHN) on the fuel properties and exhaust emissions of a single-cylinder, four-stroke, direct injection diesel engine. EHN was added to improve the cetane number of the fuel blend. The engine tests were carried out at full throttle and different engine speeds (1200–2400 rpm). The results show that the viscosity and density of the PB10PN10E1 blend (10 vol% of palm biodiesel + 10 vol% of pentanol + 1 vol% of EHN) are the lowest compared with those for diesel, and PB10 (10 vol% of palm biodiesel), and PB10PN10 (10 vol% of palm biodiesel + 10 vol% of pentanol), which improves fuel spray atomization. In addition, the cetane number, oxidation stability at 110 °C, and flash point are the highest for the PB10PN10E1 blend. The carbon monoxide and unburned hydrocarbon emissions are the lowest for the PB10PN10 blend, though the values do not differ significantly for the PB10PN10E1 blend. The smoke intensity values are the lowest for the PB10PN10E1 blend at all engine speeds. Even though the NO_x emissions are the lowest for diesel, the values do not differ significantly from those for the biodiesel blends. The biodiesel blends tested in this study can be used directly in a diesel engine without any modifications. Furthermore, cetane improvers of 20% ethyl hexyl nitrate oil can be a potential alternative fuel for diesel engines and in line with other European Union rules and other global adopted emission regulations.

1 INTRODUCTION

Energy plays a vital role in our daily life, and it is widely used in various industries ranging from agriculture and mining to construction and transportation. Fossil fuels are the major fuel in the transportation industry. Fossil fuel reserves account for 26–27% of the total energy consumption and may be entirely replaced by biofuels by 2050 (Imdadul et al., 2015). Biodiesels produced from plant oils or animal fats have garnered significant attention from researchers as an alternative to fossil fuels owing to their benefits: environmental friendliness, sustainability, biodegradability, high flash points, and

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high cetane numbers (Murugesan et al., 2009). Conversely, some biodiesels have poor physicochemical properties such as high viscosities, low volatilities, and poor cold flow properties, which lead to problems in diesel engines. The poor physicochemical properties lead to ignition delays and large quantities of carbon deposits in the diesel engine (Basha et al., 2009). For this reason, a small concentration of biodiesel or bioalcohol (typically 10 vol%) is blended with diesel in order to improve the physicochemical and cold flow properties, and the fuels can be used directly in diesel engines without any modifications (Atmanli et al., 2014). However, lower carbon alcohols such as methanol and ethanol are disadvantageous because microemulsion tends to form at lower temperatures due to separation (Atmanli et al., 2015). In addition, the poor lubricity, low cetane numbers, and low heating values of lower carbon alcohols prohibit the direct use of these fuels in diesel engines (Campos-Fernandez et al., 2013). The use of long-chain alcohols such as butanol and pentanol blended with diesel has recently drawn considerable attention from researchers due to their higher miscibility with diesel (Atmanli et al., 2015; Yilmaz et al., 2014). Imdadul et al. (2016) studied the fuel properties, performance, emissions, and combustion characteristics of a diesel engine fuelled with pentanol-biodiesel-diesel blends. Lapuerta et al. (2007) found that blending pentanol with diesel improves the calorific value and cetane number of the treated mixture (Lapuerta et al., 2007). Alcohol-based mixtures have remarkably reduced the carbon monoxide (CO) and unburned hydrocarbon (HC) emissions as well as smoke intensity compared with biodiesel-diesel blends. However, there was a slight increase in the nitrogen oxide (NO_x) and carbon dioxide (CO_2) emissions. Li et al. (2015b) investigated the combustion and emission characteristics of a diesel engine fuelled with diesel-biodiesel-pentanol blends. They found that the inherent nature of alcohols (lower viscosity and high volatility) improves the atomization characteristics of biodiesel blends (Kumar et al., 2013). In addition, diesel-biodiesel-pentanol fuel blends resulted in low soot and NO_x emissions, especially at low and intermediate engine loads. The CO emissions were found to be greatly reduced owing to the presence of oxygen in the fuel blends, and the HC emissions were the lowest at low engine loads (Li et al., 2015b). Wei et al. (2014) investigated the emissions of diesel-pentanol fuel blends and they claimed that the best volume ratio for pentanol-diesel fuel blends is 3:7. The addition of pentanol improves the in-cylinder combustion characteristics; however, this comes at the expense of higher nitrogen dioxide (NO_2) emissions. (Li et al., 2015a) found that pentanol improves premixed combustion and the resistance to engine knocking compared with diesel; however, this is negated by the lower cetane number of the fuel (Li et al., 2015a). The benefits of using higher concentrations of alcohol in diesel engines have attracted the attention of many researchers, but many claimed that fuel blends with higher alcohol concentrations will result in higher exhaust emissions at certain engine loads. The lower cetane number of alcohol fuel blends can be solved by adding a cetane improver additive. It is important to improve the cetane number as this will promote the oxidizing characteristics of the fuel blend (Li et al., 2014). To date, there is a paucity of studies concerning the use of ethyl hexyl nitrate (EHN) as a cetane improver additive in pentanol-diesel-biodiesel blends. Hence, the aim of this study is to investigate the effects of blending diesel with 10 vol% of palm biodiesel, 10 vol% of pentanol, and 1 vol% of EHN on the fuel properties and exhaust emissions of a single-cylinder, four-stroke, direct injection diesel engine. It is believed that the findings of this study will provide insight on how the addition of pentanol and EHN affects the fuel properties (viscosity at 40 °C, density at 20 °C, calorific value, cetane number, and flash point) as well as exhaust emissions (NO_x, HC, and CO emissions, and smoke intensity), which will be useful to other researchers in this field.

2 METHODOLOGY

2.1 Materials

The palm oil was sourced from the Forest Research Institute Malaysia. The chemicals used to produce the palm biodiesel were anhydrous sodium sulphate (NA_2SO_4), methanol (CH_3OH), and potassium hydroxide (KOH). Filter paper was used to filter the biodiesel from foreign particles and impurities. Pentanol and EHN were purchased from Nacalai Tesque, Inc. and Sigma-Aldrich, respectively.

2.2 Biodiesel Properties

The biodiesel production process and characterization of diesel, palm methyl ester (palm biodiesel), and biodiesel blends were carried out at the Tribology Laboratory, Department of Mechanical Engineering, University of Malaya. Three fuel blends were prepared in this study, namely, (1) PB10 (10 vol% of biodiesel), (2) PB10PN10 (10 vol% of

Table 1: List of instruments used to measure the properties of the test fuels.

Property	Instrument	Manufacturer	Model	Standard	Accuracy
Viscosity	Viscometer	Anton Paar, Austria	SVM 3000	ASTM D445	±0.1 mm^2/s
Density	Viscometer	Anton Paar, Austria	SVM 3000	ASTM D127	±0.1 kg/m^3
Flash point	Pensky-Martens flash point tester	Normalab, France	NPM 440	ASTM D93	±0.1 °C
Calorific value	Semi-automatic bomb calorimeter	Perr, USA	6100EF	ASTM D240	Up to 12000 calories/charge
Oxidation stability	873 Rancimat	Metrohm, Switzerland	873 Rancimat	EN 14112	±0.01h

biodiesel + 10 vol% of pentanol), and (3) PB10PN10E1 (10 vol% of biodiesel + 10 vol% of pentanol + and 1 vol% of EHN). The physicochemical properties of the fuels used in this study were examined in accordance with the ASTM 6751 and EN 14214 standards. The instruments used to measure the properties of the fuels are presented in Table 1.

2.3 Test Engine

The exhaust emissions of a single-cylinder, four-stroke, direct injection diesel engine were measured at the Heat Engine Laboratory, Department of Mechanical Engineering, University of Malaya. Fig. 1 shows the test engine set-up, and the specifications of the test engine are listed in Table 2. The test engine was connected to an eddy current dynamometer and data acquisition system. The dynamometer was used to measure and adjust the engine speed while the data acquisition system was used to observe and record the exhaust emissions using Dynomax 2000 software. K-type thermocouples were used to measure the temperature of the lubricating oil, water cooler, exhaust gas, and inlet air. The fuel flow rate was controlled by using Kobold ZOD positive-displacement-type flow meter. There are two separated fuel tanks; one was filled with diesel while the other was filled with the fuel blend.

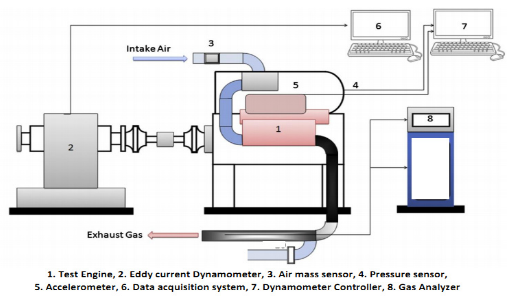


Figure 1: Schematic of the single-cylinder, four-stroke, direct injection diesel engine test bed.

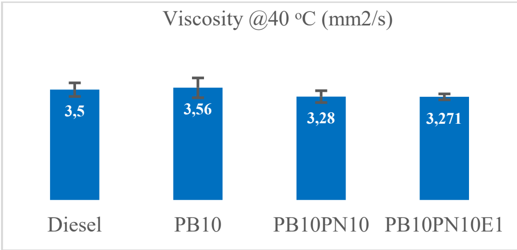
Table 2: Specifications of the single-cylinder, four-stroke, direct injection diesel test engine.

Engine model	Yanmar TF 120M
Number of cylinders	Single
Bore × stroke	92 mm × 96 mm
Displacement	0.638 L
Compression ratio	17.7:1
Maximum power	7.7 kW
Maximum engine speed	2400 rpm
Cooling system	Water cooling
Injection system	Direct injection
Injection timing	17.0 BTDC
Injection pressure	200 kg/cm^2

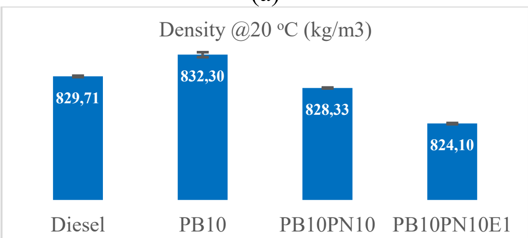
3 RESULTS AND DISCUSSION

3.1 Fuel Properties

Variations in the fuel properties due to the addition of pentanol and EHN are shown in Figs. 2–4. It can be seen from Fig. 2 that although the PB10 blend has a higher kinematic viscosity and density compared with diesel, the addition of pentanol decreases the kinematic viscosity and density for the PB10PN10 and PB10PN10E1 blends, which will promote the atomization efficiency (Li et al., 2015b). The kinematic viscosity decreases by 7.86 and 8.12% for the PB10PN10 and PB10PN10E1 blends, respectively, relative to that for the PB10 blend. The density decreases by 0.26 and 0.52% for the PB10PN10 and PB10PN10E1 blends, respectively, relative to that for the PB10 blend. This indicates that the addition of pentanol and EHN reduces the kinematic viscosity at 40 °C and density at 20 °C.



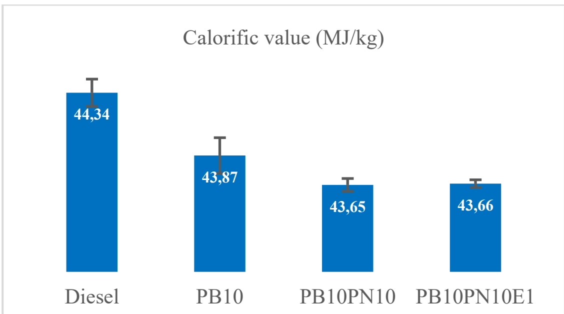
(a)



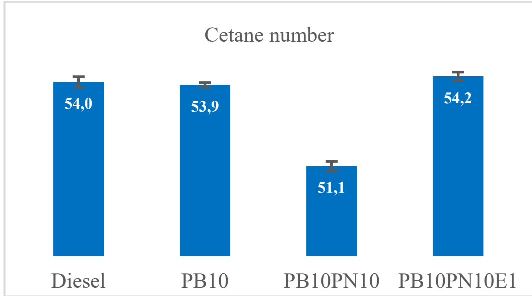
(b)

Figure 2: (a) Kinematic viscosity at 40 °C and (b) density at 20 °C of the test fuels.

The calorific value of alcohol is relatively lower, and therefore, the calorific values of the PB10PN10 and PB10PN10E1 blends are lower by ~0.5% than those of other test fuels, as shown in Fig. 3. The addition of EHN results in a slight increase in the calorific value. The cetane number of the PB10PN10 blend is lower than that of the PB10 blend by 5.2%. However, the cetane number increases by 6% for the PB10PN10 blend compared with that for the PB10 blend, indicating that the addition of EHN boosts the cetane number of the diesel-biodiesel-alcohol fuel blend.



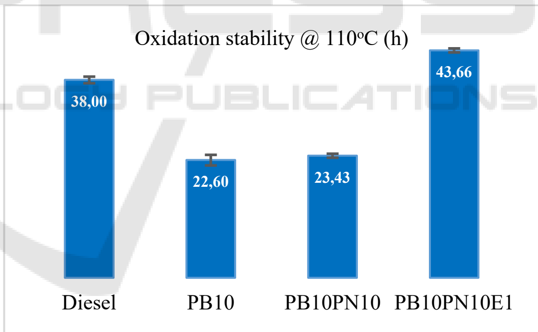
(a)



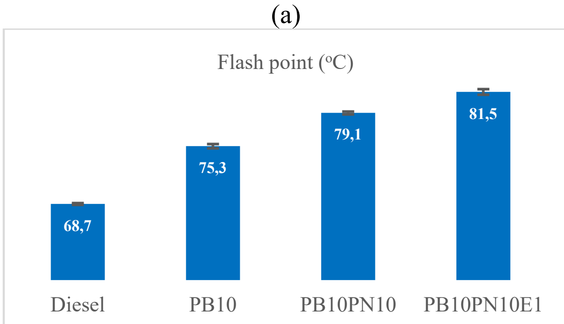
(b)

Figure 3: (a) Calorific value and (b) cetane number of the test fuels.

Fig. 4 shows the oxidation stability at 110 °C and flash point of the test fuels. In general, the PB10 blend has a lower oxidation stability than diesel. The addition of pentanol increases the calorific value by 3.1%, as demonstrated by the results for the PB10PN10 blend. The addition of EHN significantly improves the oxidation stability by 9.44%, as indicated by the result for the PB10PN10E1 blend. The flash point increases as more constituents are added into the palm biodiesel. The addition of pentanol (PB10PN10) and EHN (PB10PN10E10) increases the flash point by 5.05 and 3.03% relative to that for PB10, respectively.



(a)



(b)

Figure 4: (a) Oxidation stability at 110 °C and (b) flash point of the test fuels.

3.2 Exhaust Emissions

3.2.1 NO_x Emissions

Fig. 5 shows the NO_x emissions of the diesel engine fuelled with the test fuels with respect to the engine speed. Although the NO_x emissions for the PB10 and PB10PN10 blends are higher relative to those for diesel, the addition of EHN slightly reduces the NO_x emissions. The results show that the NO_x emissions increase by 1.60 and 6.74% for the PB10PN10 fuel blend relative to those for PB10 and diesel, respectively. When the palm biodiesel is blended with pentanol, the NO_x emissions are higher owing to the presence of oxygen atoms in the fuel blend. The properties of pentanol (low viscosity, low density, and high volatility) enhance the combustion characteristics, but this comes at the expense of higher NO_x emissions (Imdadul et al., 2016). In contrast, the addition of EHN slightly reduces the NO_x emissions, as demonstrated by the results for the PB10PN10E1 blend. The NO_x emissions decrease by 1.9% for the PB10PN10 blend relative to that for the PB10PN10 blend. Introducing EHN into the fuel blend reduces the NO_x emissions owing to changes in the cylinder peak temperature as well as low heat release rate (McCreath, 1971). EHN consists of nitrogen atoms, which will react during combustion and produce more NO_x. The addition of EHN in the fuel blend increases the cetane number, which shortens ignition delay, and reduces the time for the fuel to combust. The expansion phase during the combustion process is higher for the test fuel with higher cetane number. The combustion process is more efficient for the test fuel with higher cetane number, where the combustion takes place at a lower combustion temperature, and this reduces the NO_x emissions (Goldsborough et al., 2015; McCormick et al., 2003). In addition, NO_x emissions relatively increase with the increase of biodiesel concentration in the test fuel and a similar result was found by Yesilyurt et al. (2018). The addition of pentanol does not reduce the NO_x emissions; however, the addition of EHN gives a more favourable result. The NO_x emissions are also dependent on the adiabatic flame temperature and ignition period (Rami et al., 2021).

3.2.2 HC Emissions

Fig. 6 shows the HC emissions of the diesel engine fuelled with different test fuels with respect to the engine speed. It can be observed that the HC emissions are lower for the PB10, PB10PN10, and PB10PN10E1 test fuels compared with those for diesel. The HC emissions of the PB10PN10 reduce by 26.92 and 18.03% relative to those for PB10 and diesel, respectively. Biodiesels promote a more complete combustion owing to their oxygenative nature (Nayak et al., 2021). The addition of pentanol further promotes combustion, which reduces the HC emissions compared with the biodiesel blend. However, the addition of EHN (PB10PN10E1) slightly increases the HC emissions by 4.18% compared with the PB10PN10 blend. The addition of EHN reduces the temperature in the combustion chamber due to its cooling effect. While the cetane improver boosts the cetane number and ignition quality (reduced time for fuel-air mixing), the cetane improver slightly increases the production of HC as it slows down the oxidation process (Li et al., 2014).

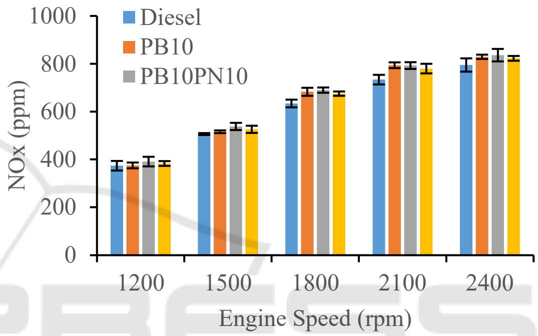


Figure 5: NO_x emissions of the diesel engine fuelled with different test fuels with respect to the engine speed.

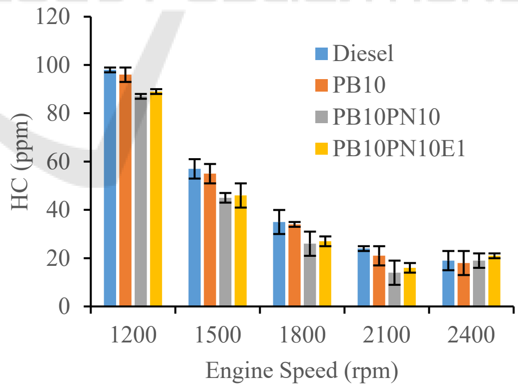


Figure 6: HC emissions of the diesel engine fuelled with different test fuels with respect to the engine speed.

3.2.3 CO Emissions

The CO emissions of the diesel engine fuelled with different test fuels are shown in Fig. 7. It is evident that the CO emissions decrease significantly with an increase in the engine speed. In addition, the CO emissions are the lowest for the PB10PN10 blend compared with those for the other test fuels. The CO emissions for the PB10PN10 blend decrease by 9.5 and 17.2% compared with those for the PB10 and diesel, respectively. The addition of pentanol improves the combustion rate by reducing incomplete combustion in the cylinder (Ma et al., 2021; Yesilyurt et al., 2018). The addition of pentanol increases the availability of oxygen atoms in the test fuel, which promotes a more complete combustion. The biodiesel blend with low carbon/hydrogen (C/H) ratio results in lower CO emissions (Qi et al., 2014). The density of pentanol is significantly lower compared with that of diesel, and thus, the volatility of pentanol is much higher, which reduces the length of spray atomization. The fuel blend containing pentanol converts into a gaseous state more quickly in the engine cylinder, promoting a more complete combustion, and reduces CO emissions (Yao et al., 2010). However, the addition of EHN into the PB10PN10 blend slightly increases the CO emissions by 2.3%. The addition of EHN decreases the hydroperoxyl (HO_2) and hydrogen peroxide (H_2O_2), and these molecules will negatively affect the oxidation of hydroxyl (OH) group and CO. The EHN results in a higher equivalence ratio, which disrupts the stoichiometry of the combustion mixture (Rashed et al., 2016).

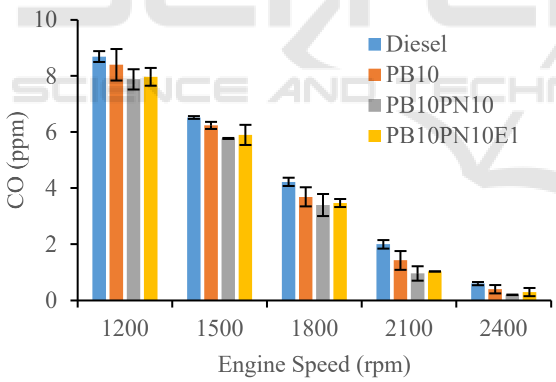


Figure 7: CO emissions of the diesel engine fuelled with different test fuels with respect to the engine speed.

3.2.4 Smoke Intensity

For a rich fuel-air mixture with a high equivalence ratio (i.e., a high actual fuel-air ratio divided by the stoichiometric fuel-air ratio), there is inadequate oxygen to convert the fuel into CO_2, resulting in the formation of CO and smoke. The smoke intensity is dependent on the type of fuel and engine operating conditions such as the engine load and speed. Fig. 8 shows the smoke intensity of the diesel engine fuelled with different test fuels with respect to the engine speed. In general, the PB10PN10E1 blend has the lowest smoke intensity, followed by the PB10PN10, PB10, and diesel test fuels, regardless of the engine speed. The PB10, PB10PN10, and PB10PN10E1 blends have a lower smoke intensity compared with diesel due to the presence of oxygen atoms in the fuel-rich zone during the early stage of the PC phase. This eventually reduces the formation of smoke (Ozsezen et al., 2008). The smoke intensity decreases if the impurities of the biodiesel are in small quantities and the sulphur content is low (Teoh et al., 2013). Pan et al. (2019) and Sebayang et al. (2017) found that the addition of pentanol decreases soot formation compared with that for diesel and biodiesel blends (Pan et al., 2019; Sebayang et al., 2017). The addition of EHN further reduces the soot formation, as evidenced by the results of the PB10PN10E1 blend. The smoke intensity for the PB10PN10 blend decreases by 19.60 and 17.18% relative to those for the PB10 and diesel, respectively. The smoke intensity for the PB10PN10E1 blend reduces by 8.24% relative to that for the PB10. In general, the smoke intensity is lower at the initial stage of the premixed combustion phase because the fuel-air mixture is nearest to the stoichiometric state. The oxygen content is significantly higher during the fuel-rich state for the PB10, PB10PN10, and PB10PN10E1 blends, which results in lower smoke emissions compared with diesel. The higher cetane number of the PB10PN10E1 blend promotes early combustion, which gives sufficient time for soot oxidation to occur and reduces smoke formation (Imtenan et al., 2015). Moreover, blending the diesel and biodiesel with pentanol and EHN reduces the viscosity, which improves fuel atomization, and reduces the smoke intensity (Rakopoulos et al., 2007).

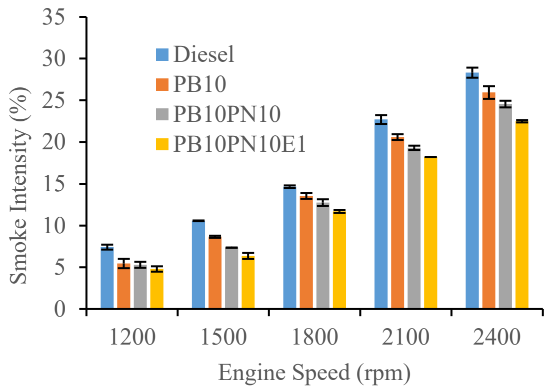


Figure 8: Smoke intensities of the diesel engine fuelled with different test fuels with respect to the engine speed.

4 CONCLUSIONS

The objective of this study is to investigate the effects of blending diesel with 10 vol% of palm biodiesel, 10 vol% of pentanol, and 1 vol% of EHN on the fuel properties and exhaust emissions of a single-cylinder, four-stroke, direct injection diesel engine. The engine tests were carried out at full throttle and different engine speeds. The results were compared with those for neat diesel, and PB10 and PB10PN10 blends. It is found that the viscosity and density are lower upon the addition of pentanol, but these properties are compensated for upon the addition of EHN. EHN is a cetane improver, which improves the oxidation stability of the PB10PN10E1 blend. The calorific value is reduced for the PB10PN10 blend, but is slightly increased for the PB10PN10E1 blend. The NO_x emissions are higher for the PB10PN10 blend, but the NO_x emissions are slightly reduced for the PB10PN10E1 blend. The HC and CO emissions exhibit a declining trend with an increase in engine speed, with the lowest values obtained for the PB10PN10 blend. However, the addition of EHN results in a slight increase in the HC and CO emissions, as evidenced by the results for the PB10PN10E1 blend. The smoke intensities of the PB10, PB10PN10, and PB10PN10E1 blends are also lower compared with those for diesel.

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