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Influence of additives to biodiesel-diesel blend on a modern tier-4 turbo-charged diesel engine's idling emissions

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Abstract
This study focuses on investigating the effects of several additives on diesel engine's idling emissions. Experiments using a modern (Tier-4) 4-cylinder direct injection (DI) diesel engine were investigated at two idling speeds. The fuels investigated were B0, B40 and B100. Four additives, namely methanol, ethanol, diethyl ether (DEE) and water were mixed with B40 blend. The engine tested from cold start to warm-up conditions, and the average results were analyzed. The engine's fuel consumption, exhaust gases temperature (EGT), and regulated emissions were investigated. The regulated emissions investigated were oxides of nitrogen (NO_x), carbon monoxide (CO), unburned hydrocarbon (HC) and smoke opacity. All additives improved NOx and smoke emissions compared to its base fuel.

Keywords: Modern diesel engine; Idling condition; Biodiesel; Additives; Emissions.

1. Introduction

The growing worldwide energy demand is directly attributed to the rising global population. In line with this increased energy demand, multiple energy sources have been explored with emphasis shifting towards greener energy. Until recently, energy used globally was derived primarily from carbon-based fuels. Diesel engines are commonly used in many applications due to their high conversion efficiency and economic power source. However, dependency on diesel fuel contributes to the pollution of the environment since the main emissions from diesel engine are carbon monoxide (CO), nitrogen oxides (NO_x), unburned hydrocarbon (HC), and particulate matters (PM). As a result, multiple alternatives have been proposed, one of which being biodiesel, which has been largely touted as a viable alternative for fueling diesel engines.

Biodiesel is mono alkyl esters of long chains of fatty acids that are derived from several lipid feed stocks such as vegetable oil. Biodiesel could easily fuel diesel engines with simple or no modifications to the engine. Compared to diesel, biodiesel generally has improved (higher) cetane number (CN) and flash point, whereas biodiesel's heating value is lower than that of conventional diesel [1-3]. Moreover; biodiesel molecules have a presence of oxygen (10-11%), which causes more complete combustion [4]. Burning biodiesel in a diesel engine results in lower CO, HC, and PM emissions compared to conventional diesel [5, 6]. It is not, however, without blemish, as biodiesel is largely associated with high NO_x emissions [7, 8].

Much work has been done to control diesel engines' NO_x emissions. Such potential is an exhaust gas recirculation (EGR) system. Generally, EGR system works by recirculating a portion of the diesel engine's exhaust gases back into the cylinder to replace a certain percentage of oxygen, hence a lower combustion temperature. Wang et al. [9] conducted research on a 2-stroke diesel engine using the EGR system, and reported that increasing the EGR rate up to 40% significantly reduces NO_x emission by about 75%. Kumar et al. [10] studied the effect of EGR on constant speed diesel engine fueled with pentanol diesel blends, and achieved a 57% reduction of NO_x emission with 30% EGR rate and a blend of 30% pentanol with diesel. Yasin et al. [11] indicated that using EGR with a diesel engine reduces both combustion temperature and NO_x emission. Another approach to reducing combustion temperature was noted by introducing water into the engine, whether as a steam into the intake air system, or into the fuel as emulsion fuel. Kokkuiunk et al. [12] conducted theoretical and experimental investigations of steam injection into a diesel engine, and concluded that NO_x emission dramatically decreased with a slight increase in specific fuel consumption. Elsanusi et al. [13] investigated the effect of fuel emulsion on diesel engine regulated emissions with various levels of water content in the emulsion; they obtained significantly low NO_x emission with the highest water content in emulsified fuel.

There are many studies that proposed that some additives can be blended with diesel or biodiesel to improve their properties and control exhaust emission. The most common additives currently used in combination with diesel and biodiesel fuel are oxygenated additives such as methanol [14], ethanol [15], butanol [16], and acetone [17]. There is contradiction about those additives' effects on NO_x emission formation. Some researchers indicated that high oxygen content and lower CN of those additives resulted in higher combustion temperature, which led to increased NO_x formation [18-20]. On the other hand, some researchers reported that latent heat of vaporization and lower adiabatic flame of the blends that contain such additives are the main reason for reducing in-cylinder temperature, hence lower NO_x formation [21-23].

Since there are contradicting results regarding the effect of oxygenated additives on diesel engine regulated emission, this work experimentally investigates the effects of various additives that have different latent heat of vaporization on a heavy-duty diesel engine's regulated emissions under two idling conditions. Additionally, a CN improver is proposed in order to improve the CN of the blend. The additives proposed include methanol, ethanol, water (emulsion fuel), and DEE.

2. Experimental setup

2.1 Material

The materials used in this study are: low-sulfur diesel, canola oil, sodium hydroxide pellet, methanol, ethanol, DEE, water, Sorbitan Monoleate (Span 80) and Polyoxyethylene Sorbitan Monoleate (Tween 80).

2.2 Biodiesel production

Biodiesel produced in the lab using the transesterification method, which is simply a chemical reaction of oil and alcohol with the help of a catalyst that accelerates the reaction to produce biodiesel [24, 25]. The method of producing biodiesel is started by mixing the two components: sodium hydroxide (which acts as the catalyst) and methanol. These are added to the mixture of 200 ml methanol and 3.5 gm of catalyst. They are both placed in an air-tight container and mixed until the catalyst is properly dissolved. The canola oil is heated to 60°C, after which the mixture of methanol and catalyst are added in the blender. This solution is then left to blend at high speed for at least 50 minutes so they are adequately mixed. The speed of the blender should be high enough to properly mix the contents. During blending, the process is monitored at regular intervals to check the temperature, because the boiling point of the methanol is approximately 65°C. Therefore, the temperature of the mixture should be below that point. When the single-phase solution is ready, it is poured into a 2-litre bottle and kept for one day. After 24 hours, 2 major products are formed: glycerin, which is known as the by-product of biodiesel, and biodiesel itself. By separating the glycerine and washing the biodiesel twice, a final biodiesel product was obtained. The volumetric collection efficiency of biodiesel was calculated to be approximately 80%, and its quality under ASTM 6751 can be found in Table 1.

2.3 Selection of fuels and fuel blends

In this study, ultra-low sulfur diesel and canola biodiesel were used as the main fuels. The diesel and biodiesel were blended by a volumetric ratio of 40% biodiesel and 60% diesel (B40). The proposed additives to B40 are ethanol, methanol, DEE and water, and their addition by volumetric percentage is 15.

The ethanol, methanol and DEE were added to blend B40 with normal mixing. When adding water, the emulsifying process was required in order to obtain stable emulsified fuel. Emulsion fuel is a blend of immiscible liquids with emulsifiers [13, 26, 27]. The emulsified fuel was prepared using the external force method. In this method, a blend of Span 80 and Tween 80 were stabilized at Hydrophile-Lipophile Balance (HLB) 8, and their addition to fuel in a volumetric percent was 2% [28, 29]. Distilled water was added to the fuel in a volumetric percentage of 15%, and by running the mixer at 6000 rpm for 15 minutes to obtain emulsion B40 with 15% of water (EB40W15). Another emulsified fuel as prepared using the same volumetric percentages, but this time, 15 vol. % of DEE added to obtain EB40WDEE15. The results were milky emulsified fuels, and their properties are shown in Table 2.

Table 1. Canola biodiesel properties.

Test Name	Test Method	ASTM limit	Results
Free Glycerin (mass%)	ASTM D6584	Max. 0.02	0
Total Glycerin (mass%)	ASTM D6584	Max. 0.24	0.112
Flash Point, Closed Cup (^{0}C)	ASTM D93	Min. 130	169
Water & Sediment (vol.%)	ASTM D2709	Max. 0.050	0
TAN (mg KOH/g)	ASTM D664	Max. 0.5	0.14
Sim. Dist., 50% recovery (^{0}C)	ASTM D2887	N/A	359.8
Cetane Index	ASTM D976 (2 variables formula)	N/A	50
Copper Corrosion, 3h @ 50^{0}C (rating)	ASTM D130	Max. 3a	1a

Table 2. Fuel properties and compositions.

Name/symbol	Composition	H.V (kJ/kg)	Density (kg/m^3)	Viscosity (cSt @ 40°C)	CN	Latent heat of vaporization (kJ/kg)
B0	Diesel	44890	827	1.97	48	232
Methanol	Methanol	18200	791	0.69	5	1167
Ethanol	Ethanol	29700	800	0.80	5-8	921
DEE	Diethyl ether	36892	710	0.23	125	368
W	Water	0	1000	0.66	-	2260
Span 80	Sorbitan Monoleate	-	990	(@ 25°C) 1000-2000		-
Tween 80	Polyoxyethylene Sorbitan Monoleate	-	1000.9	(@ 25°C) 300-500		-
B100	Biodiesel	40523	889	4.21	50	200-250
B40	(60 vol.% Diesel, 40 vol.% B100)	42763	849	2.89	-	-
EB40W15%	(85 vol.% B40, 15 vol.% water)	36264	878	4.66	-	-
EB40WDEE15%	(70 vol.% B40, 15 vol.% water, 15 vol.% DEE)	36071	863	4.42	-	-
B40M15	(85 vol.% B40, 15 vol.% methanol)	39217	839	2.39	-	-
B40E15	(85 vol.% B40, 15 vol.% ethanol)	39453	841	2.61	-	-
B40DEE15	(85 vol.% B40, 15 vol.% DEE)	40021	833	1.90	-	-

2.4 Engine under study

A heavy-duty Cummins Tier-4 Final QSB4.5 inline 4-cylinder turbocharged engine was used, with a high pressure common rail injection system, and a diesel particulate filter. The engine specifications can be found in Table 3. A schematic diagram for the diesel engine is outlined in Figure 1.

Table 3. Engine specifications.

Engine Make and Model	Cummins QSB 4.5 T4I
Engine Type	Inline 4-Cylinder
Number of Cylinders	Four
Bore * Stroke	102mm * 138mm
Swept Volume	4.5 l
Compressions Ratio	17.3:1
Rated Power	97 kW @ 2300 RPM

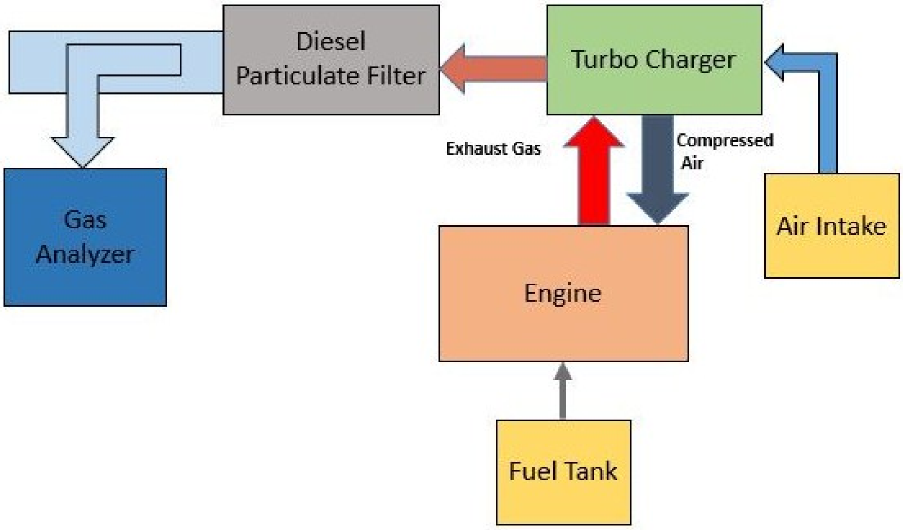

Figure 1. Schematic diagram of engine test.

2.5 Test procedure

The engine was tested at two idling speeds (1000 and 1200 rpm). Various emissions were examined from the different additives to B40 blend. The tests were conducted over 30 minutes under no load condition from a cold start. The regulated emissions (CO, HC, NO_x and smoke) were measured at different time intervals of 2, 4, 6, 8, 10, 15, 20, 25 and 30 minutes after starting the engine. For emission testing, several devices were used: NovaGas 7466K for regular emissions, a DWYER 1205A analyzer for CO emission, and a Smart 1500 opacimeter for smoke measurement. The emission measurement devices specifications are described in Table 4.

Table 4. Specifications of experimental measurement devices.

Method of Detection	Species	Measured unit	Range	Resolution	Accuracy
NovaGas 7466K					
ElectroChemical/Infrared detector	CO	%	0-10%	0.10%	±1%
Infrared Detector	CO_2	%	0-20%	0.10%	±1%
Electro Chemical	NO	ppm	0-2000 ppm	1 ppm	±2%
Electro Chemical	NO_2	ppm	0-800 ppm	1 ppm	±2%
Electro Chemical	O_2	%	0-25%	0.10%	±1%
Infrared Detector	HC	ppm x 10	0-20000 ppm	10 ppm	±1%
Dwyer 1205A					
Electro Chemical	CO	ppm	0-2000	1 ppm	±5%
ExTech EA10	Temp	0.1 ^{0}C	(-)200^{0}C to 1360^{0}C	0.1^{0}C	±0.3%
Smart 1500	Opacity Soot Density	% mg/m³	0-100% 0-10 mg/m³	0.1% 0.00001	±2% ±2%

3. Results and discussion

3.1 Fuel consumption

Figure 2 shows fuel consumption for diesel, biodiesel and B40 with various additives. The fuel consumption was found to increase with the increased engine speed, as would be expected. B100 had higher fuel consumption by 4.86% at 1000 RPM engine speed compared to neat diesel, which could be due to the lower heat content of biodiesel. All additives to B40 resulted in higher fuel consumption compared to B40, with EB40W15 having the highest fuel consumption. With respect to EB40DEEW15, all fuels with lower heat content achieved higher fuel consumption. Although EB40DEEW15 showed lower HHV (see Table 2), it averaged approximately 1.2% lower fuel consumption compared to EB40W15 at the two idling conditions, which could be due to two reasons. Firstly, DEE has very high CN, which improved the total CN of the blend; hence a lower ignition delay period and lower fuel consumption. The second reason could be because EB40DEEW15 had lower density compared to EB40W15, leading to less (kg) burned for the same volume.

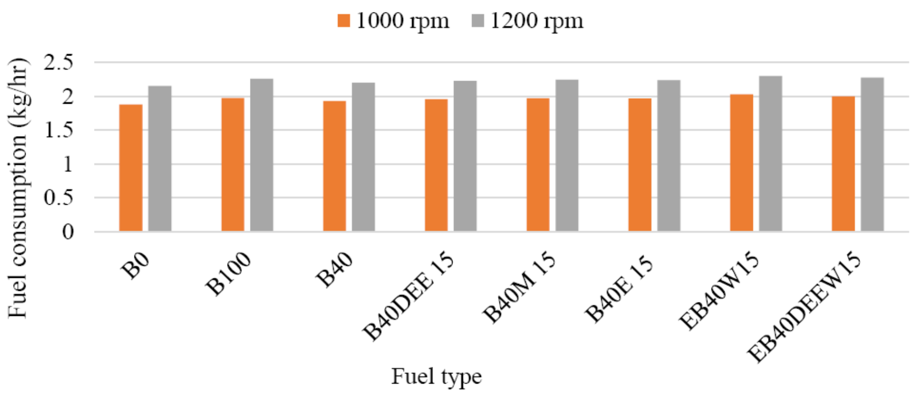

Figure 2. Fuel consumption of various fuel blends at different engine speeds.

3.2 Exhaust gas temperature

The engine design and fuel properties are two factors affecting the exhaust gas temperature of a diesel engine. Generally, higher oxygen content in the fuel results in higher EGT, whereas higher latent heat of vaporization has an opposite effect. Figure 3 depicts the average EGT of a diesel engine at 1000 and 1200 rpm with no load condition for various fuels. Among all fuels, B100 resulted in higher EGT at the two engine speeds investigated. This noted increase in EGT is mainly a result of higher oxygen content and similar latent heat of diesel vaporization. Although methanol and ethanol are oxygenated additives, they showed lower EGT compared to B0, B40 and B100. B40E15 and B40M15 provided lower EGT by 6.75% and 8.55% compared to B40 at 1200 rpm engine speed. The lower CN and higher latent heat of vaporization of those additives are the main reason for this decrease [30]; B40DEE15 had a slight increase in EGT where the DEE was CN improver. Fuel with lower CN resulted in an increase in ignition delay, hence more fuel accumulated in the combustion chamber [31]. EB40W15 had the lowest EGT among all fuels investigated compared to B40; EGT reduction was 13.5% at low speed, and 12.97% at high speed. At the onset of combustion, the amount of water in the emulsion absorbing the combustion heat led to a drop in peak flame temperature.

3.3 Emissions

3.3.1 NO_x emission

NO_x formation depends on several parameters such as engine temperature, ignition delay and fuel properties [32]. The variation in averaged NO_x emission as a function of engine speed for all fuel types is represented in Figure 4. It was observed that the NO_x emission increased when increasing the speed from 1000 to 1200 rpm; an increase of 8.67% for B0. Among all fuel types, B100 had higher NO_x emission; compared to B0, the NO_x emission was approximately 6% and 9% higher at 1000 and 1200 rpm, respectively. This is due to a high presence of oxygen in biodiesel molecules, which improved the engine combustion temperature [33, 34]. NO_x emission of B40DEE15 was slightly lower than B40 by 3.14% at 1000 rpm. The higher CN of DEE lowered the ignition delay period, which helped reduce NO_x emission [35, 36]. Methanol and ethanol additives into B40 represented lower NO_x emission than the base fuel for the two engine speed, as shown in Figure 4. This is due to the fact that the high evaporation enthalpy of methanol and ethanol reduced the combustion temperature, hence lower NO_x formation [37]. There was a significant reduction of NO_x emission when the engine was operating with EB40W15. At 1000 rpm engine speed, NO_x emission was 8.8%, 12.04% and 14.2% lower for EB40W15 than with B0, B40 and B100, respectively. The water amount in the emulsified fuel was responsible for decreasing the peak flame temperature, leading to lower NO_x emission of EB40W15 [13]. The maximum NO_x emission was observed for EB40DEEW15 at 1200 rpm engine speed as (184 NO and 33 NO_2), which was (236 NO and 40 NO_2) for B100. Additionally, EB40DEEW15 provided slightly lower NO_x emission by 1.38% than EB40DEEW15 at 1000 rpm engine speed. The main reason for this reduction is that water has zero CN by adding DEE, which has above 125 CN, which enhanced the emulsion fuel CN leading to a shorter ignition delay period.

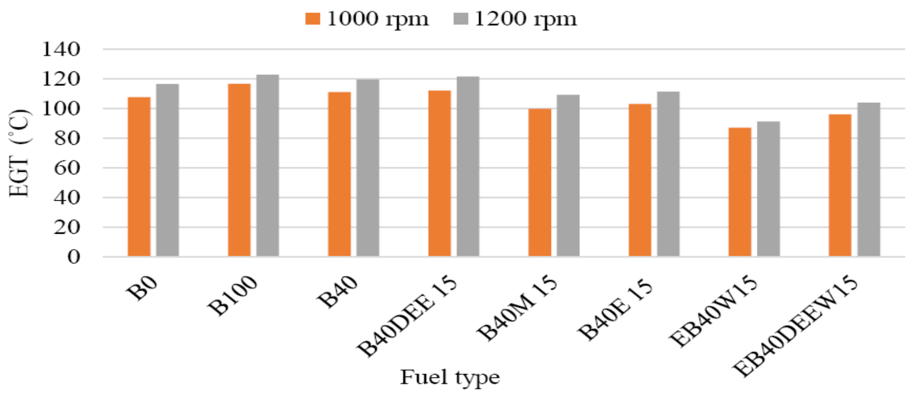

Figure 3. EGT of various fuel blends at different engine speeds.

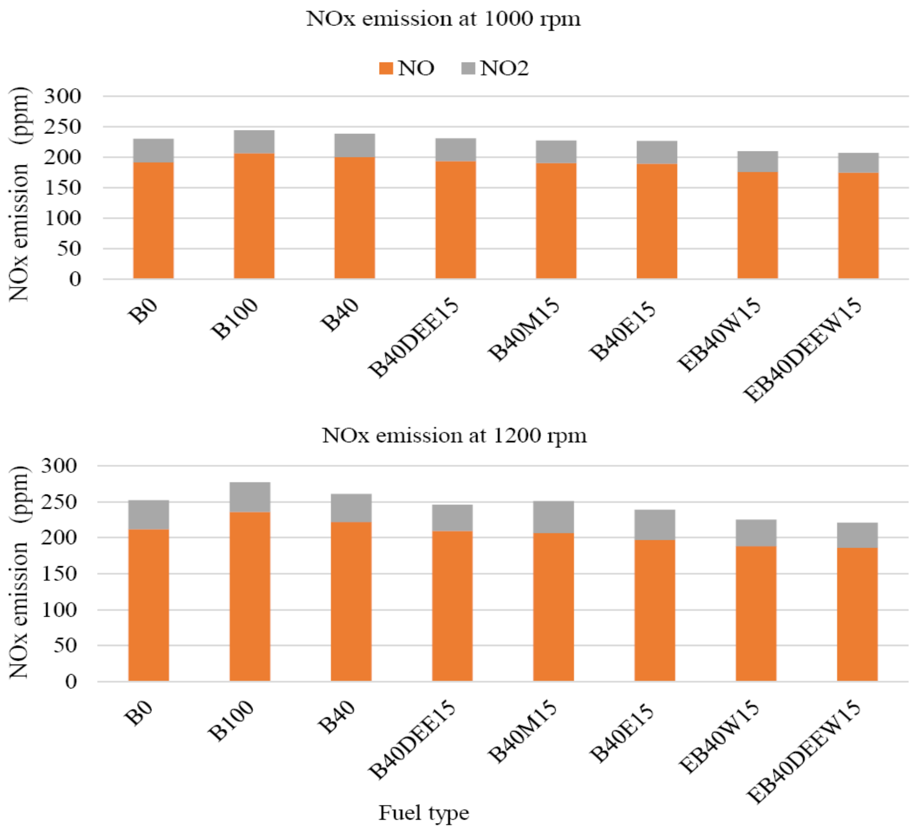

Figure 4. NOx emissions of various fuel blends at different engine speeds.

3.3.2 CO and HC emissions

Generally speaking, the incomplete combustion of fuel and insufficient oxygen presence are the main reasons for producing CO and HC emissions. In fact, B100 had lower average CO emission compared to neat diesel at both engine operating conditions (Figure 5). This reduction was observed to be 20.74% lower than that obtained from B0 at 1000 rpm engine speed. Another observation was that an increase in engine speed decreased CO emission, which could be due to the fact that increasing the combustion temperature (which was presented in Figure 3) attributed to oxygenated CO forming CO_2 emission. Figure 5 depicts variations of CO emission at different speeds for several additives, including B40. B40M15 and B40E15 were found to have higher CO emission than the base fuel. At 1200 rpm, B40M15 and B40E15 CO emission were 7.85% and 6.33% higher respectively, than B40. Even though methanol and ethanol are oxygenated additives, the low CN and high evaporation enthalpy of methanol and ethanol were responsible for the poor oxidation reaction rate of CO, leading to incomplete combustion, hence the formation of more CO. Blending DEE to B40 provided 7.1% and 9.1% lower CO emission than B40 at 1000 and 1200 rpm, respectively. DEE had low latent heat of vaporization and very high CN, as well as high oxygen content leading to acceleration of the reaction rate of CO to form more CO_2. The highest CO emission observation was from EB40W15 among all fuels investigated, which was 17.15% higher than B40 at 1200 rpm engine speed. The very high latent heat of vaporization, as well as its low CN, were the main reasons of this increase. However, adding DEE to the emulsion fuel was found to improve the fuel. As a result, EB40DEEW15 had lower CO emission (11.557% and 5.29%) than EB40W15 and B40M15, respectively, at 1000 rpm engine speed.

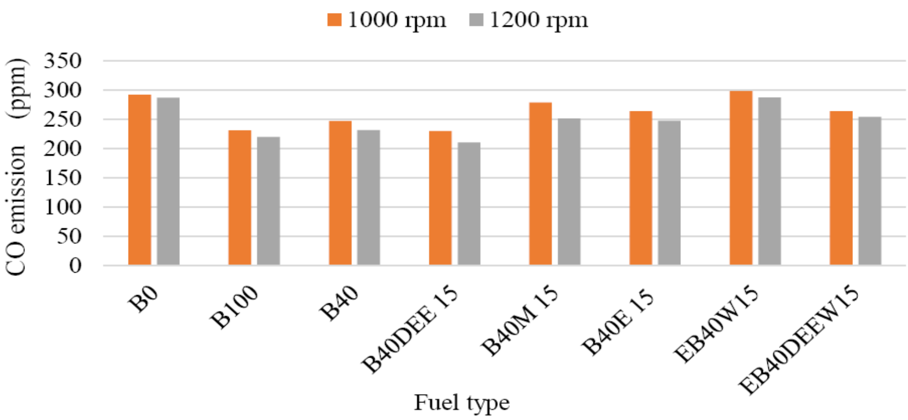

Figure 5. CO emissions of various fuel blends at different engine speeds.

The average HC emission variation as a function of engine speed for different fuel blends is shown in Figure 6. Generally, incomplete combustion caused by very rich or very lean air-fuel ratio, flame quenching in cold region around the cylinder, and heat loss, are the main reason for HC emission [38]. The oxygenated additives methanol and ethanol attributed to higher HC emission due to lower EGT and consequent incomplete combustion. Therefore, B40M15 and B40E15 had slightly higher HC emission than B40 at the two idling conditions. The EB40DEEW15 produceed higher HC emission among all fuels investigated at two idling conditions (12.963% higher than B100 at engine speed of 1200 rpm). The reason for this increase in HC emission could be attributed to the presence of water in the emulsion, which led to a long ignition delay period. DEE addition to the emulsion enhanced its CN, whereby a shorter ignition delay was obtained, leading to lower HC emission, as observed from EB40DEEW15. Although the HC emission of EB40DEEW15 was 3.7% less than that obtained from EB40W15, it still showed higher HC emission than the other fuels investigated.

3.3.3 Smoke opacity

Figure 7 shows the average smoke opacity variation at engine speeds for different fuel blends. The optical properties of fuel smoke are measured by smoke opacity. The viscosity and oxygen bond of fuel are the main factors affecting smoke opacity [39]. The smoke opacity of all additives was found to be lower than their fuel bases. B40DEE15, B40E15 and B40M15 provided lower smoke opacity by 19%, 14.28% and 10%, respectively than B40 at 1000 rpm engine speed. The reason for this reduction could be due to the fact that additives reduce fuel viscosity and enhance combustion quality. At 1200 rpm engine speed, EB40W15 presented 28.57% lower smoke opacity than B40. The significant smoke intensity reduction was obtained from EB40DEEW15 by about 38% than from B40 at 1200 rpm engine speed. The improved fuel mixing and fuel atomization, as well as emulsion micro-explosion, were the main reasons for smoke opacity reduction of emulsified fuel.

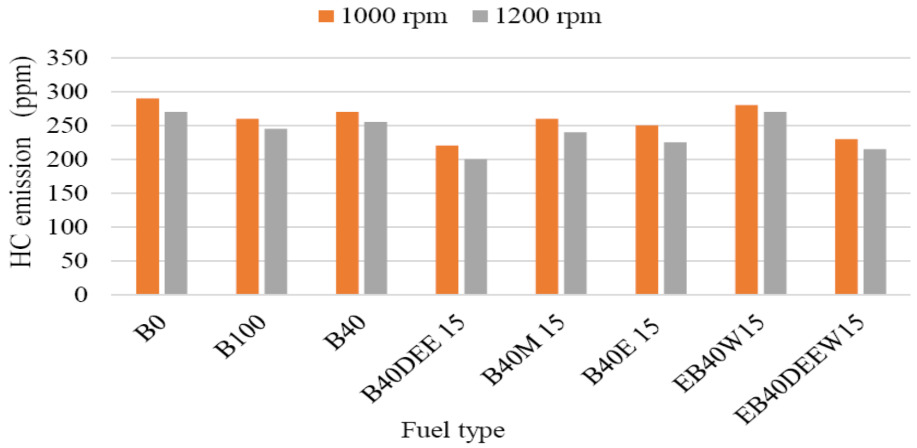

Figure 6. HC emissions of various fuel blends at different engine speeds.

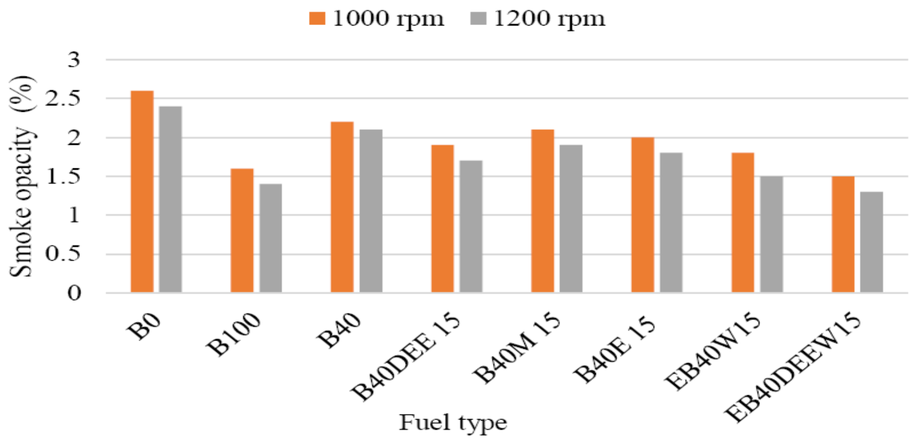

Figure 7. Smoke emissions of various fuel blends at different engine speeds.

4. Conclusion

Ethanol, methanol, DEE and water additives to B40 were used for testing diesel engine emission at two idling conditions. The results were compared with B0, B40 and B100, and the conclusions from the experimental study were drawn as follows:

1. All fuels with additives showed higher fuel consumption compared to B0, B40 and B100. EB40W15 had the highest fuel consumption by 6.35%, 4.22% and 1.6% compared to B0, B40 and B100, respectively, at 1200 rpm engine speed.
2. All fuel additives provided lower EGT, with EB40W15 having the lowest EGT by 21.97% compared to B40 at 1000 rpm engine speed.
3. Biodiesel represented higher NO_x emission than diesel by approximately 6% and 9%, at engine speed conditions of 1000 and 1200 rpm, respectively. Methanol, ethanol, DEE and water additives showed lower NO_x emission compared to all fuels investigated. The greatest reduction of NO_x was provided by EB40DEEW15 (20.22% less than B100) at 1200 rpm engine speed.
4. B40DEE15 showed similar results of CO emission as that obtained from B100 at the two idling conditions; both had lower CO emission than all other fuels investigated. Methanol, ethanol, and water tended to have higher CO emission than all other fuels tested, with the greatest CO emission obtained from EB40W15. However, the addition of DEE to the emulsion fuel resulted in reducing the CO emission to be somehow equivalent to that obtained from B40E15 and B40M15.
5. B100 provided lower HC emission than all fuels investigated, while the additives to B40 provided slightly higher HC than B0, B40 and B100. The highest HC emission showed by EB40W15, whereas the addition of 15% DEE to this fuel reduced the HC emission to give results closer to that of B40.
6. The fuels with additives resulted in lower smoke opacity than their bases. EB40DEEW15 showed the lowest smoke compared to all fuels investigated, which was 38% lower than B40 at 1200 rpm engine speed.

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