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Detailed Analysis of PAH Formation, Toxicity and Regulated Pollutants in a Diesel Engine Running on Diesel Blends with n-Propanol, n-Butanol and n-Pentanol

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Abstract: There are a number of emissions produced by internal combustion engines that are regulated to limit atmospheric pollution. However, it is equally important for both environmental and human health to also monitor and control polycyclic aromatic hydrocarbons (PAHs). Using high-carbon alcohols with straight-chain structures, such as n-propanol (Pro), n-butanol (Bu) and n-pentanol (Pen), together with diesel fuel (D), can be a way to reduce these harmful pollutants. In this study, nine different test fuels were created by mixing each higher alcohol with diesel fuel at 5%, 20% and 30% mixing ratios. In order to compare the effects of these test fuels on regulated pollutants and PAH compounds, fuel blends were evaluated in a diesel engine at partial loads and at a constant speed. Regulated emissions were measured using a standard 5-gas analyzer, and PAHs were detected and quantified using rigorous analytical chemistry methods, such as gas chromatography–mass spectrometry (GC–MS). While higher carbon monoxide (CO) and hydrocarbon (HC) pollutants were emitted by the binary blends due to their high oxygen content and latent heat of evaporation (LHE), a decrease in nitrogen oxides (NO_x) emissions between 4.98% and 20.08% was observed depending on the alcohol concentration. With the exception of the 20% n-pentanol mixture, PAH concentrations in the exhaust gas were significantly reduced in other binary blends. The 35% n-butanol mixture stood out in reducing total PAHs by 80.98%. In toxicity reduction, the 20% n-propanol mixture was the most effective with a decrease of 91.23% in toxicity. Overall, higher alcohols have been shown to be effective additives not only in reducing overall PAH emissions and toxicity, but also in reducing high-ring and heavier PAHs, which are more carcinogenic and cause a greater risk to engine lifedue to wet stacking under cold starting or low-load conditions.

Keywords: diesel engine; higher alcohol; blend ratio; regulated emissions; PAHs; wet stacking

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1. Introduction

The necessity of utilizing alternative fuels in compression ignition engines has become more urgent in both the transportation and power generation sectors [1]. This need is caused by two issues: the first is the decrease in oil reserves along with price instability, and the other is emission regulations aimed at environmental preservation and human health [2]. Despite the high efficiency of diesel engines, NO_x, HC and CO are leading pollutants emitted by diesel fuel [3]. Currently, various measures are taken in diesel engines to reduce these emissions that are subject to regulations such as EU norms. Among such measures, the utilization of alternative fuels has become critical due to the high cost of modifications to diesel engines, increasing oil prices and decreases in oil reserves [4].

Ideal alternative fuels to consider for use in diesel engines should be easily produced and accessible, and not adversely affect the environment and food safety [5]. Bioalcohols and biodiesel are such leading alternative fuels utilized in compression ignition

engines [4,6]. Due to the difficulties experienced in obtaining raw materials for biodiesel, bioalcohols that can be economically produced from all kinds of agricultural wastes have become more advantageous [6]. Bioalcohols are at the forefront of alternative fuels that can meet the aforementioned conditions and be used in a diesel engine without making any modifications to the engine [7,8]. Bioalcohols can be produced from many kinds of local industrial, agricultural and forest waste using existing alcohol production processes [9,10].

Methanol (CH_3OH) and ethanol (C_2H_5OH), which are low-carbon alcohols, have not been developed for utilization in diesel engines due to their poor properties and phase separation problems at low temperatures [11]. The combustion performance and solubility of alcohols improve with the number of carbon atoms in their chemical structure [12,13]. In recent years, C3 and higher carbon alcohols have gained increasing attention among researchers for further evaluation and assessment. Among these alcohols, straight-chain n-pentanol ($C_5H_{11}OH$), n-butanol (C_4H_9OH) and n-propanol (C_3H_7OH) stand out in terms of availability and efficiency [14,15]. They are considered among the most promising alternatives for diesel engines [9]. Miscibility of these bioalcohols with diesel fuel ensures the highest possible biofuel usage in diesel engines and the potential to reduce diesel fuel consumption. The raw materials used to produce these high-carbon alcohols can be sourced from recycling and waste [16]. For this reason, such alcohols can be utilized to support environmental protection and economic development. In addition, their superior fuel properties (e.g., higher cetane number, lower LHE, higher heat of combustion), proportional to the number of carbons, put them at the forefront in comparison to low-carbon alcohols [16,17].

While the current literature has a few studies regarding n-butanol and n-pentanol, there are even fewer investigations for n-propanol [16,18]. In a study performed by Sen [19], smoke and NO_x emissions decreased with a mixture containing 15% n-propanol by volume and diesel. Muthaiyan et al. tested diesel blends with propanol (10–25% volume percentages) and determined these propanol–diesel blends result in lower thermal efficiency and produce less CO, NO_x and smoke emissions [20]. Balamurugan et al. examined 4% and 8% propanol–diesel mixtures in a diesel engine and observed lower CO and NO_x with propanol blends [21]. Regarding n-butanol–diesel mixtures, Pan et al. investigated 10% and 20% n-butanol–diesel mixtures under different injection conditions [22]. With a higher n-butanol mixing ratio, NO_x emissions increased with a strong dependency on the oxygen content and temperature increase. Tipanluisa et al. found that 10% n-butanol with diesel showed the best performance in terms of NO_x reduction and combustion performance, compared to 5% and 20% blends [23]. Chen et al. examined diesel with 10%, 20% and 30% ratios of n-butanol, ethanol and methanol mixtures [24]. After the addition of all three alcohols, different results were obtained in the NO_x emissions of binary mixtures. Wei et al. blended 30% pentanol with diesel, which led to lower HC and CO pollutants at high engine loads along with lower NO_x and particulates, but higher HC and CO at low engine loads [25]. In several investigations conducted by Yilmaz et al., 1-pentanol and diesel blends resulted in substantially lower NO_x, but higher CO and HC pollutants [26–28]. Ma et al. noted that the oxygen content of pentanol in diesel–pentanol blends resulted in a small reduction in soot, but also a small increase in natural flame brightness [29]. In all studies on diesel and high-carbon alcohol mixtures, lower NO_x emissions and partially higher HC and CO emissions have been observed, with a strong dependency on the alcohol concentration in the mixture [30–33].

The reduction in regulated pollutants, such as HC, CO and NO_x, are heavily considered while utilizing alternative fuels in diesel engines [34–36]. However, examining the correlation between alternative fuels and unregulated PAH emissions that may be more dangerous than the regulated emissions provides additional insights regarding the advantages of utilizing these fuels [37]. PAHs have also long been designated as carcinogens by both the International Agency for Research on Cancer (IARC) and the US Environmental Protection Agency (EPA) [38,39]. Of these, thousands of PAHs are structurally possible, but the EPA has identified 17 as priority compounds for environmental control [39]. Further-

more, as a result of the cold running and long-term operation of the diesel engine at low loads, a wet stacking problem arises due to high aromatic formation, which negatively affects the durability of the engine [40]. However, no studies exist examining PAH formation with diesel–n-propanol or diesel–n-pentanol blends. In addition, there are very limited studies investigating the role of n-butanol and diesel blends on PAH formation. Gowtham et al. [41] examined the effects of 10%, 20% and 30% n-butanol fumigation on PAH formation. A slight increase in high cyclic aromatics was detected with the higher n-butanol ratio in fumigation. Arias et al. [42] reported carbonyl and PAH emissions of 13% and 20% n-butanol from renewable diesel mixtures. The mixture with 13% n-butanol by volume produced the highest carbonyl compound emissions. Although low-ring PAH emissions were mostly detected in both mixtures, an increase was observed in some high-ring PAHs. As can be seen from these limited studies, there is a knowledge gap regarding the effects of diesel and high-carbon alcohol blends on PAH emissions.

Increasing the use of high-carbon alcohol together with diesel fuel, in conjunction with a sufficient comparative examination of the pollutants emitted by such diesel blends, is important for sustaining the environment, human health and the operating life of diesel engines. Therefore, this comparative study of the effects of these three alcohol types on PAH formation contributes to a better understanding of their role on the environment and engine durability. To that end, this study tests nine different test fuels created by blending diesel with n-propanol, n-butanol and n-pentanol at concentrations of 5%, 20% and 35%. NO_x, CO, HC and PAH (total PAH, PAH dispersion and toxicity) emissions of these test fuels in a diesel engine were determined and compared with baseline diesel in detail.

2. Materials and Methods

2.1. Engine Test Conditions and Test Fuels

A four-cylinder, indirect-injected Onan DJC diesel engine was tested at different engine loads from idle to 9 kW under a constant engine speed (@1800 rpm). Table 1 shows specifications of the engine, along with the experimental test setup, including PAH sampling (as shown in Figure 1). No modifications to the engine were performed other than the inclusion of an auxiliary fuel tank for the test fuels. The fuel mass consumption was measured by comparison of the mass of fuel before and after each 20-min trial for the fuel at each engine load. The fuels used in this study included standard diesel (No. 2) and high-carbon alcohols (n-propanol (CAS No:71-23-8), n-butanol (CAS No:71-36-3) and n-pentanol (CAS No:71-41-0), which were obtained from Merck. Nine different mixtures named DPro, DBu and DPen were formed with 5%, 20% and 35% mixing ratios of high-carbon alcohols. Select fuel properties for each test fuel are listed in Table 2. Engine emissions were determined using a 5-gas analyzer (Model: EMS 5002-5) for which measurement ranges and resolutions of HC, CO and NO are given in Table 3. For experimental confidence and repeatability, tests were repeated three times for each experimental sample according to the ISO 8178-6:2018 standard.

Table 1. Technical specifications of test engine.

Engine Type	Onan Diesel Generator
Bore (mm)	82.55
Stroke (mm)	92.08
Displacement (cm^3)	1970
Number of cylinders	4
Number of cycles	4 cycle
Compression ratio	19:1
Max rating output (kW)	12
Max rating speed (rpm)	1800
Intake system	Natural aspirated
Fuel injection pump	PSU type
Fuel injection system	Indirect
Injection pressure (MPa)	13.1
Injection timing (bTDC)	18 °CA

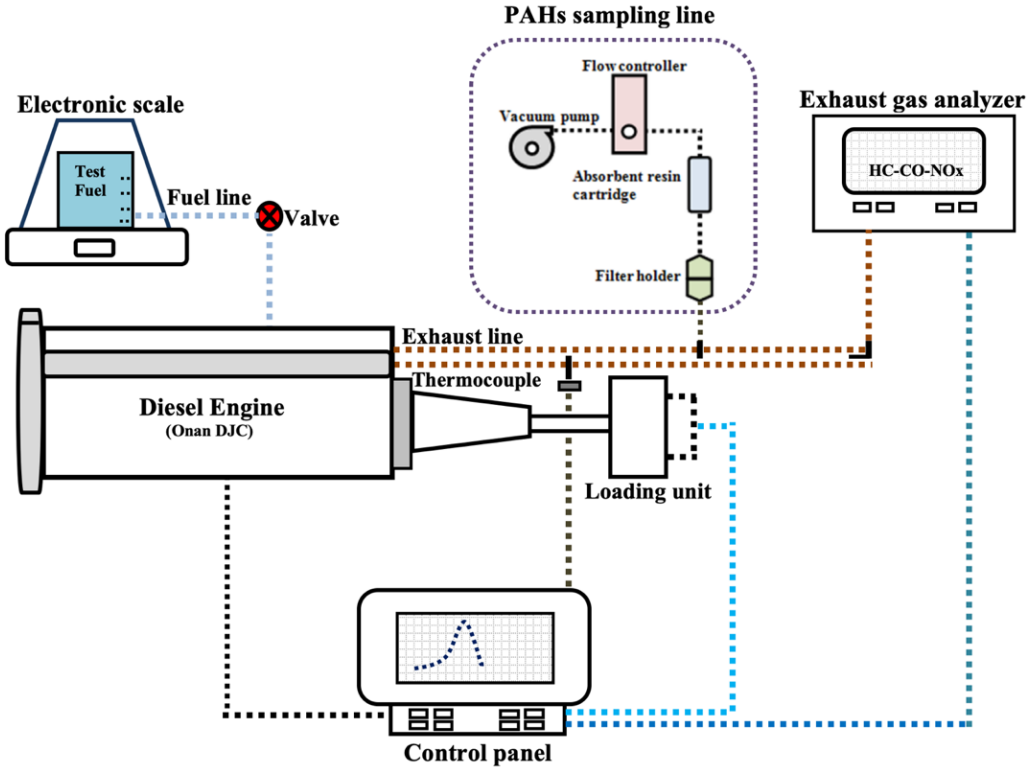

Figure 1. Experimental facility.

Table 2. The basic chemical properties of test fuels.

	ASTM Test Methods						
	D4052-91	**D240**	**D613**	**D445**	**D93-94**	**D2500-91**	**D6371-05**
Fuels	**Density (g/mL)**	**Lower Heating Value (MJ/kg)**	**Cetane Number**	**Kinematic Viscosity (mm^2/s) @ 40 °C**	**Flash Point (°C)**	**Cloud Point (°C)**	**CFPP (°C)**
Diesel fuel	0.818	44.81	54.5	2.95	76.12	−12	−20
n-propanol	0.803	30.63	12	1.74	22	-	≤−51
n-butanol	0.810	33.10	17	2.23	35	-	≤51
n-pentanol	0.815	34.65	20	2.89	49	-	−40
DPro5	0.813	43.72	51.21	2.65	46.25	−15	−21
DBu5	0.817	44.25	52.15	2.90	67	−16	−22
DPen5	0.817	44.30	52.30	2.94	62.12	−15	−22
DPro20	0.809	41.86	44.13	2.42	44.58	−18	−22
DBu20	0.814	42.80	46.35	2.78	59	−18	−24
DPen20	0.813	42.35	45.50	2.90	50.26	−18	−23
DPro35	0.805	39.10	40.00	2.11	42.73	−21	−25
DBu35	0.813	41.00	41.13	2.69	54	−21	−27
DPen35	0.811	41.40	42.10	2.88	49.98	−21	−24

Table 3. The measurement ranges and resolutions of the quantities.

Item	Quantity	Range	Accuracy
Rotary encoder	Speed	0–6000 rpm	±1 rpm
Loading unit (Electrical resistance)	Load	1000/5000 W	±5 W
Exhaust gas analyzer	HC	0–2000 ppm	±4 ppm
	CO	0–10 vol.%	±0.06 vol.%
	NO	0–5000 ppm	±25 ppm

2.2. PAH Emissions Sample Collection and Analysis

The test engine was operated at idle with diesel for approximately ten minutes to minimize cold start effects. In order to collect PAH samples, the test engines were then run at idle speed for three hours with each fuel type, and this procedure was repeated three times. Undiluted exhaust samples were collected at ten liters per minute (L/min) via a series of collection channels on which PAHs were concentrated. Figure 1 shows the sampling line where aromatic hydrocarbons were gathered in an adsorbent resin cartridge with two collection media linked in series. A two-stage Amberlite XAD-2 adsorbent resin (50 mg/100 mg) was used to fill the resin cartridge. The temperature throughout the filter was controlled to not exceed 50 °C, on average. The resin cartridges and filter were separately spiked with anthracene-d10, which works as an internal control for isotope dilution mass spectrometry. Subsequently, aromatic hydrocarbons were extracted into 5 mL of HPLC-grade n-hexane, aspirated from a purification column and washed with an additional 5 mL of n-hexane. Activation was completed at 120 °C for 24 h prior to use. PAHs were then recovered with 50/50 vol% HPLC-grade benzene/acetonitrile and concentrated using nitrogen blowdown. The solutions were kept at −80 °C until the next analysis. Following the selected ion monitoring (SIM) process, the gas chromatography–mass spectrometry (GC–MS) which used helium as a carrier gas, was utilized to detect and quantify PAHs. Specifications of the GC–MS system are shown in Table 4. Sample collection and analysis of PAH emissions were determined for standard diesel and higher alcohol blends according to the EN ISO 11338-2:2003 test standard.

Table 4. Thermal Program GC–MS.

Instrument Details	**GC–MS: HP 5890/5971A** **Column: DB5-MS**
Injection volume	1 µL
Injection temperature	300 °C
Thermal program	Hold 70° for 1 min Heat from 70–200 °C @ 70 °C/min Hold 200 °C for 2 min Heat 200–300 °C @ 7 °C/min Hold 200 °C for 10 min

3. Results and Discussions

For each test engine, regulated pollutants and unregulated compounds, such as change in NO_x, CO, HC, total PAHs, PAH dispersion and PAH toxicity, were evaluated and compared among diesel and blended fuels. Results are discussed in terms of regulated and unregulated emission parameters, with emphasis on the formation of PAHs.

3.1. Regulated Emissions

3.1.1. NO_x Emissions

NO_x is produced as a reaction of nitrogen in air with oxygen at high temperatures. In this regard, the combustion chamber temperature and air/fuel ratio are two important parameters affecting NO_x formation [4,43,44]. As shown in Figure 2, higher temperatures

are reached near the end of combustion, because diesel has a high cetane number and calorific value: a rise in NO_x emissions is observed throughout the entire load range. With the addition of high-carbon alcohols to diesel, a reduction in the NO_x emissions of all binary mixtures, varying between 4.98% and 20.08%, was obtained. The primary reason for this decrease is a longer ignition delay time and lower in-cylinder temperature caused by a lower cetane number and higher LHE values of alcohols [11,29,45]. Chemical reaction rates are important in alcohol blends, but these rates also depend on temperature [3,10]. The local NO formation in the spray from diesel combustion was affected by the local concentration of the oxygen molecules and the flame temperature [25]. The results of this study are similar to other studies on diesel alcohol mixture in the literature [26,27,29].

When evaluated together with the fuel properties in Table 2, a small difference was observed in the reduction in NO_x in binary mixtures with the same mixing ratios. Among the binary blends, these reductions were as follows for low-to-high alcohol concentrations: DBu (6.77%–9.59%–20.08%), DPro (5.88%, 8.14%, 18.3%) and DPen (4.98%–6.7%–16.52%). As the alcohol concentration in the mixture increased, higher reductions in NO_x emissions were observed, and the maximum reduction was obtained from the DBu35 mixture at 20.08%.

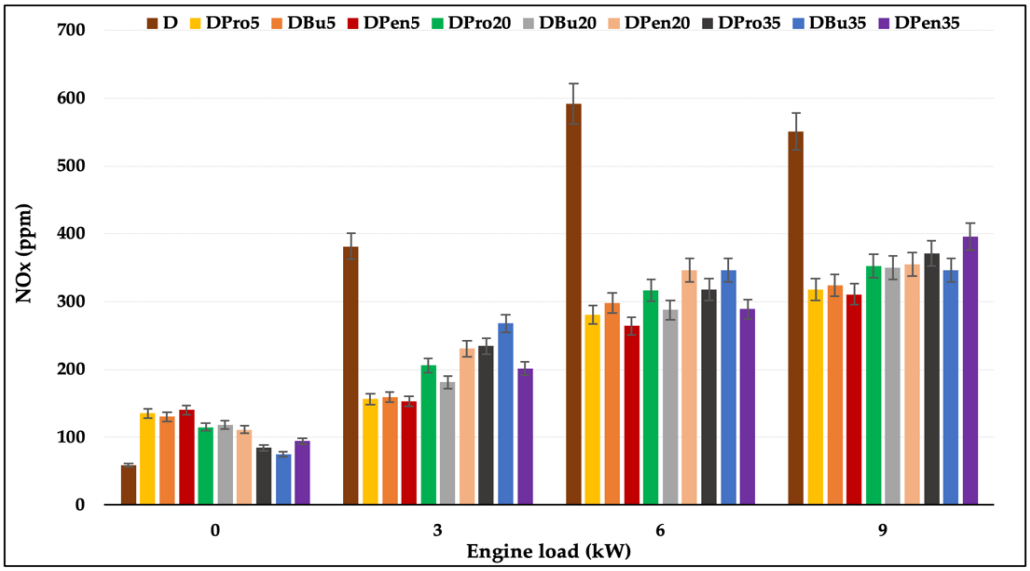

Figure 2. Comparison of NO_x emissions with engine load for test fuels.

3.1.2. CO Emissions

As shown in Figure 3, while the CO emissions produced by diesel fuel was high in the no-load condition, it had a decreasing trend with higher loads. The main reason for the presence of CO among combustion products is the result of incomplete combustion with insufficient oxygen [45,46]. When considering the entire combustion chamber, oxygen may be insufficient in general, and if the mixture is not completely homogeneous, local excess oxygen in a certain location of the combustion chamber may cause the flame to die out and not fully complete combustion [46]. Thus, when higher alcohols were added to diesel fuel (except DBu5), an increase was observed in the average CO emission of all mixtures. This increase is listed as DBu < DPro < DPen from least to most. As compared to diesel, an increase of 79.68%, 66.01% and 93.35% was recorded in the mixtures of DPro35, DBu35 and DPen35, respectively. With higher alcohol concentrations, a significant increase in CO emissions was observed because of low in-cylinder temperatures and rapid flame extinction [26,27]. Additionally, the presence of higher alcohols in the fuel promotes a higher ignition delay and creates fuel-rich zones in the cylinder, which lead to higher CO formation [20,21]. However, slight reductions occurred due to the increase in the conversion rate of CO to CO_2 in the DBu5 mixture. Therefore, in general, the use of low-rate high-

carbon alcohol with diesel fuel can be considered as a method to reduce CO emissions in the literature [23,24,28].

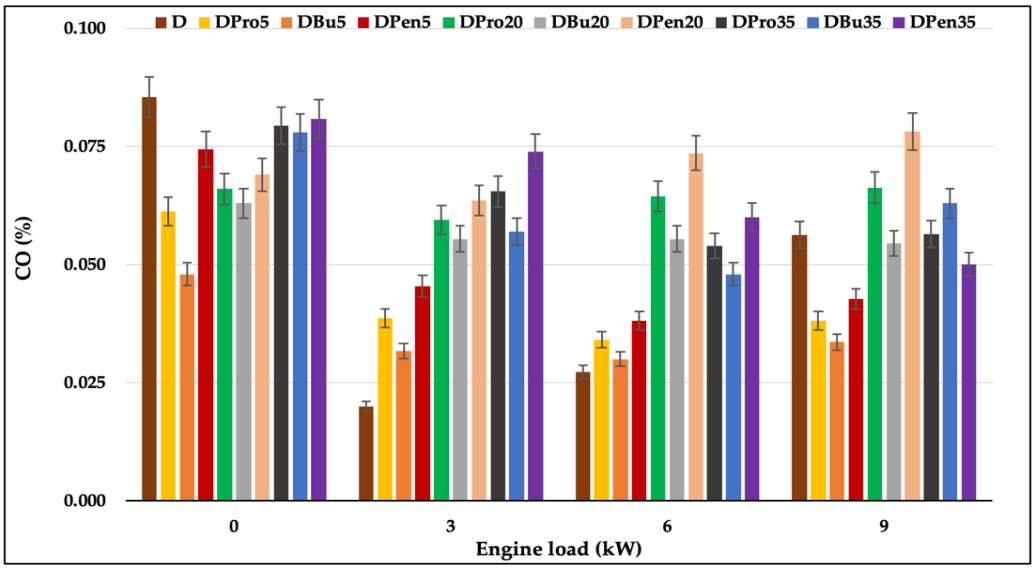

Figure 3. Comparison of CO emissions with engine load for test fuels.

3.1.3. HC Emissions

HC formation is a result of incomplete combustion [47]. Engine design, operating conditions, injection characteristics, fuel properties and air/fuel ratio are the main parameters that govern incomplete combustion [47,48]. Similar to CO emissions, emissions of HC were found to be lower than those of binary mixtures, as shown in Figure 4. Depending on the increased oxygen ratio in the cylinder, other factors such as flame extinction, misfires, partial burns and oil absorption in the cylinder may cause HC emissions as a result of incomplete combustion [49,50]. Among the 5% mixtures, HC emissions increased as follows: DPro5 (110.48%) < DPen5 (123.46%) < DBu5 (159.40%). For the 20% concentration volume of the test fuels, HC emissions were produced, least to greatest, as follows: DPro < DBu < DPen. As the alcohol content increased in the mixtures, the increase in HC emission drastically increased. The DBu < DPro < DPen ranking was obtained at a mixing ratio of 35%. These differences between alcohols were the result of the radicals on combustion of each alcohol. The maximum increase was obtained with the DPen35 mixture. This trend can be ascribed to higher LHE and lower cetane numbers of blended fuels [44]. These characteristics create a quenching effect and a wider lean outer-flame zone, both of which cause higher unburned hydrocarbons [42]. Higher HC emissions with respect to higher alcohol content in diesel/alcohol blends is an outcome consistent within the literature [24,28,33].

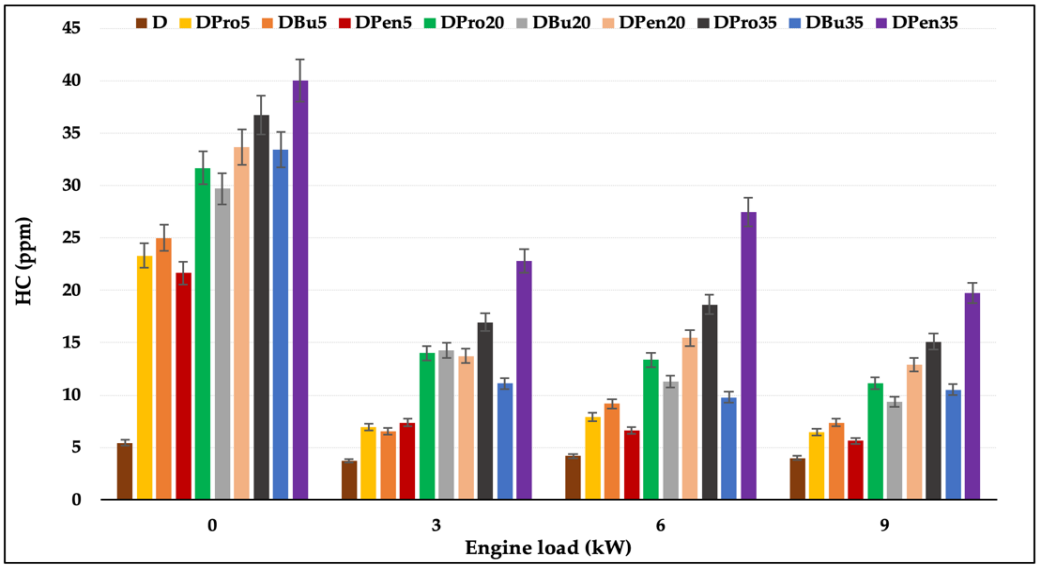

Figure 4. Comparison of HC emission with engine load for test fuels.

3.2. Unregulated Emissions

3.2.1. PAH Concentration in Exhaust Gas

The PAH emission concentration (μg/m^3) in the exhaust gas is given in Figure 5, and the total PAH concentrations are tabulated in Table 5. Due to the chemical nature of diesel fuel, it is likely to emit PAH components [51,52]. The total PAH concentration of diesel fuel, mostly naphthalene (two-ring) and phenanthrene (three-ring), was obtained at 4.73 μg/m^3. When Figure 5 is viewed in terms of diesel, it is clearly seen that diesel leads to significantly higher PAH emissions compared to binary blends. When n-pentanol, n-butanol and n-propanol were added to diesel, significant reductions were obtained in the total PAH emissions of all blends (except DPen20). With the addition of alcohol, the total concentration of high-ring aromatic compounds also decreased. The order of this reduction is DPro5 (71.20%) > DBu5 (66.86%) > DPen5 (0.59%) in the 5% mixtures. Among these mixtures, 5% n-pentanol addition resulted in a slight decrease, while an increase was observed in the 20% mixture, which may be caused by the higher cetane number and chemical kinetics of pentanol. On the other hand, in the 35% mixture, the PAH emission reduction order was determined as DBu (80.98%) > DPro (61.50%) > DPen (42.02%). The LHE effect of alcohols and the cooling effect of the -OH group caused a decrease in the PAH formation reaction mechanism, which reduced total PAH emissions [53]. It has been determined that the addition of alcohol in a high mixing ratio is effective in reducing the most harmful NO_x emissions, as well as the total PAH emission concentration in a similar way [54]. The addition of alcohol in a high mixing ratio also has the effect of increasing the durability of the diesel engine, thanks to its potential to prevent wet stacking [39,51].

Table 5. PAH concentration in exhaust gas.

PAH	Number of Rings	Total PAHs (μg/m^3)									
		D	DPro5	DBu5	DPen5	DPro20	DBu20	DPen20	DPro35	DBu35	DPen35
Naphthalene	2	1.93	0.226	0.39	0.566	0.37	0.64	2.30	0.52	0.23	0.81
Acenaphthylene	2	0.21	0.012	0.27	0.670	0.13	0.26	0.76	0.37	0.33	0.42
Acenaphthene	2	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *
Fluorene	2	0.59	0.132	0.30	1.191	0.38	0.17	1.20	0.59	0.22	0.96
Phenanthrene	3	1.19	0.252	0.29	1.518	0.58	0.04	1.38	0.23	0.02	0.43
Anthracene-D10	3	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *
Anthracene	3	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *
Fluoranthene	3	0.29	0.350	0.11	0.332	0.13	0.03	0.14	0.05	0.04	0.06
Pyrene	4	0.40	0.350	0.15	0.342	0.20	0.03	0.12	0.05	0.04	0.05
Benzo[a]anthracene	4	0.00 *	0.009	0.01	0.012	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *
Chrysene	4	0.09	0.024	0.04	0.039	0.01	0.00 *	0.01	0.01	0.01	0.00 *
Benzo[b]fluoranthene	4	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *
Benzo[k]fluoranthene	4	0.00 *	0.008	0.01	0.021	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *
Benzo[a]pyrene	5	0.01	0.00 *	0.01	0.014	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *
Indeno[1,2,3-c,d]pyrene	5	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *
Dibenz[a,h]anthracene	5	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *
Benzo[g,h,i]perylene	6	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *

* undetected.

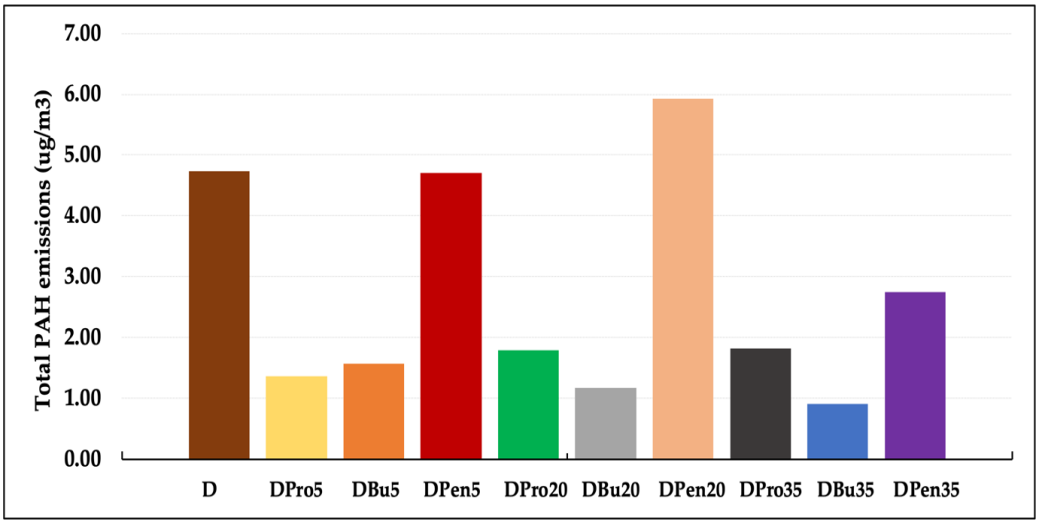

Figure 5. Total PAH emissions of test fuels.

3.2.2. Distribution of PAH

Distribution of PAHs is as equally important as the total PAH formation in exhaust gas [52,55]. An increase in the number of aromatic compounds with higher rings also increases the polluting and harmful effects of PAHs. Therefore, it is vital to reduce PAH compounds with five or more rings. Of the 17 PAHs identified as primary by the EPA, 14 were detected in these experimental studies. The remaining three compounds fell below the detection limit and are given in Table 5. Figure 6 shows the number of aromatic rings and the relative distribution of PAHs of the test fuels. The distribution of PAH emissions with diesel fuel was 57.8%, 31.3%, 10.6% and 0.3%, and consisted of two, three, four, and five aromatic rings, respectively. According to Figure 6 and Table 5, the PAH distribution of all test fuels is higher for the two- and three-ring aromatic components. The highest rates in the distribution of two-ring aromatics were determined as 61% (DBu5), 91.5% (DBu20) and 87.4% (DBu35) in n-butanol mixtures, respectively. High levels of low-ring PAHs may be due to the number of blended fuels pyrolyzed from incomplete combustion due to the addition of alcohol [53,54]. In the three-ring distribution, the lowest distribution was obtained in n-butanol mixtures. Considering the four-ring distribution, the smallest level of distribution was obtained in the n-pentanol mixtures: 8.8% (DPen5), 2.3% (DPen20) and 2.2% (DPen35), respectively. Differences existed among the alcohols for the five-ring

distribution. Five-ring aromatics were not detected in the mixtures of DPr05, DPro20, DPen20 and DPen35. However, the percentage of five-ring aromatic distribution among the other mixtures was obtained as 0.8% (DBu5), 0.3% (DPen5), 0.1% (DBu20), 0.1% (DPro35) and 0.5% (DBu35). The formation of five-ring aromatics can be ascribed to the ignition delay of alcohols in this ratio, depending on the cetane number and the inability of alcohol radicals to suppress formation in the final stage of combustion. Minimizing PAHs with higher rings in the PAH distribution prevents total PAH formation that could cause diesel engine failure such as wet stacking [40,56]. Thus, blended fuels without five-ring aromatic compounds minimize the production of higher PAHs, making blended fuels superior to diesel in terms of possible engine failures and carcinogenic effects.

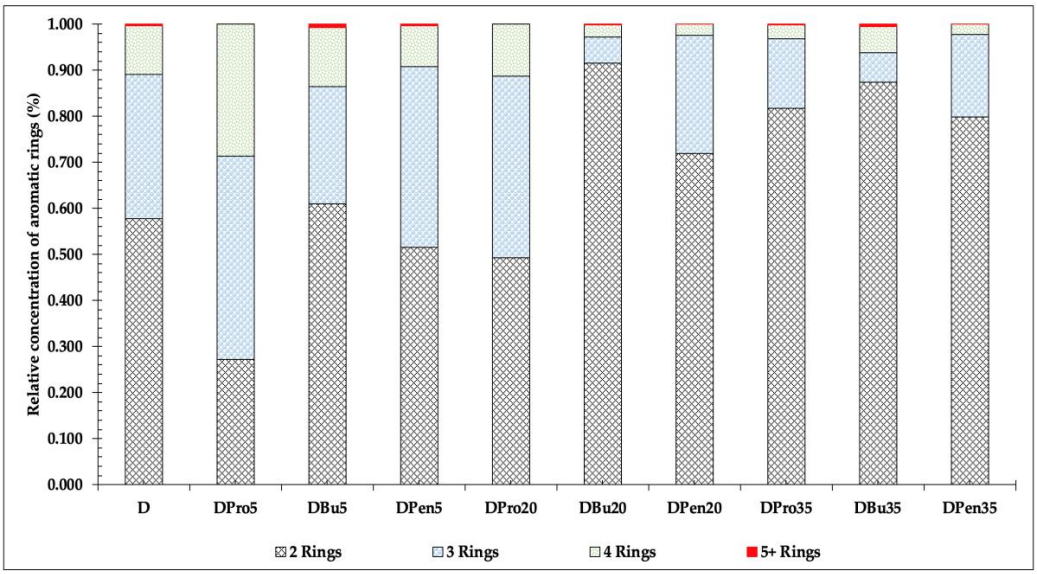

Figure 6. Relative distribution of PAH by number of aromatic rings.

3.2.3. Toxicity of PAH Emissions

Together with the total PAH formation and distribution, the toxic effect of PAHs on human and environmental health should also be examined [56,57]. The total carcinogenicity of PAHs is defined as a toxic equivalent factor (TEF) value, and the weighted benzo[a]pyrene equivalent (BaPeq) of each PAH compound was calculated based on the TEF [58]. The toxicity distribution of PAH emissions is shown in Figure 7 and the toxicity BaPeq concentration in exhaust gas is given in Table 6. Due to the chemical structure of the diesel fuel, 16.20 BaPeq ng/m^3 toxicity occurred on the basis of the TEF. The addition of high-carbon alcohol to diesel resulted in an increase in toxicity values, depending on the amount of high-ring aromatic compounds [59]. When toxicities of 5% blends are compared with diesel fuel, a decrease of 87.27% and 11.66% was observed in the DPro5 and DBu5 blends, while an increase of 19.39% was observed in the DPen5 blend. This is because five-ring benzo[a]pyrene, four-ring benzo[a]anthracene and benzo[k]fluoranthene have the highest values in DPen5 with 13.803, 1.249,and 0.207 BaPeq (ng/m^3) concentrations, respectively. n-pentanol chemical kinetics may have caused an increase in PAHs due to the incomplete reaction of various radicals [50,52,57]. Among the 20% mixtures, the smallest toxicity value was obtained in DPro20 with 1.42 BaPeq (ng/m^3). Additionally, no high-ring PAH was detected in DPro20, except for four-ring Chrysene (0.007 BaPeq). The order of the maximum reduction in toxicity in the 20% mixtures is DPro (91.23%) > DBu (87.53%) > DPen (64.49%). In the mixture ratio of 35%, the order was determined as DPen (84.34%) > DPro (75.81%) > DBu (67.29%). These reductions were due to the very low PAH level affecting BaPeq in high alcohol mixtures of 20% and 35% and the chemical composition of the mixtures. In general, the alcohol mixing ratio, together with other fuel properties (e.g., density, viscosity and cetane number), can directly affect the amount of high-molecular

PAHs that form at the end of combustion [59,60]. All these factors directly contributed to the amount of toxicity reduction among the mixtures. As a result, although all eight blends reduced toxicity compared to diesel, the negative impacts of other fuel properties on emissions should not be ignored with increased alcohol blend ratios.

Table 6. Toxicity BaPeq concentration in exhaust gas.

PAH	Number of Rings	Toxicity BaPeq (ng/m^3)									
		D	DPro5	DBu5	DPen5	DPro20	DBu20	DPen20	DPro35	DBu35	DPen35
Acenaphthylene	2	0.211	0.012	0.268	0.670	0.134	0.257	0.758	0.373	0.330	0.416
Fluorene	2	0.593	0.132	0.296	1.191	0.377	0.170	1.200	0.594	0.225	0.964
Phenanthrene	3	1.194	0.252	0.289	1.518	0.580	0.040	1.381	0.227	0.022	0.431
Fluoranthene	3	0.288	0.350	0.109	0.332	0.126	0.027	0.143	0.049	0.036	0.061
Pyrene	4	0.403	0.350	0.151	0.342	0.196	0.027	0.123	0.049	0.045	0.053
Benzo[a]anthracene	4	0.000	0.864	0.858	1.249	0.000	0.000	0.466	0.000	0.000	0.000
Chrysene	4	0.094	0.024	0.036	0.039	0.007	0.003	0.009	0.005	0.005	0.005
Benzo[b]fluoranthene	4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.053	0.000	0.107
Benzo[k]fluoranthene	4	0.046	0.077	0.054	0.207	0.000	0.011	0.024	0.008	0.000	0.016
Benzo[a]pyrene	5	13.378	0.000	12.255	13.803	0.000	1.485	1.652	2.562	4.639	0.486

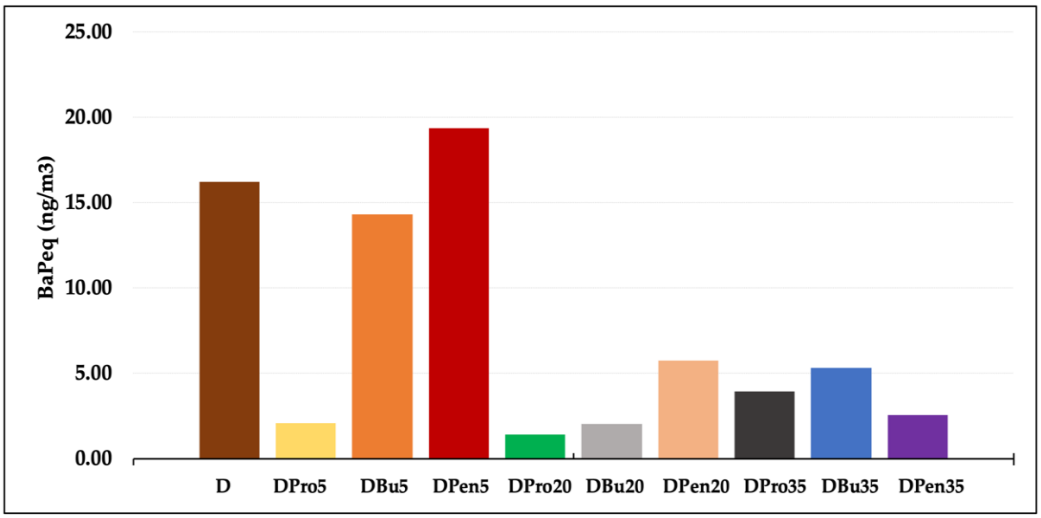

Figure 7. The toxicity distribution of test fuels.

4. Conclusions

High-carbon alcohols, such as n-propanol, n-butanol and n-pentanol, stand out as promising additives which can be produced from biomass and have superior properties over low-carbon alcohols. As the current literature has a lack of sufficient data and knowledge about the effects of diesel–alcohol blends on PAH formation, this work aimed to fill the gap by focusing on unregulated and regulated emissions of n-propanol/n-butanol/n-pentanol–diesel blends in the low- and high- mixing ratio range. Key results are listed as follows:

- With the effect of a low cetane number and LHE values of high-carbon alcohols, NO_x emissions decreased for all mixtures, with the extent depending on the alcohol ratio in the mixture. The maximum NO_x reduction among mixtures was obtained in the DBu35 mixture at 20.08%. In addition, the NO_x reduction order among all mixing ratios of 5%–20%–35% alcohol addition to diesel was determined as DBu (6.77%–9.59%–20.08%) > DPro (5.88%, 8.14%, 18.3%) > DPen (4.98%–6.7%–16.52%). Contrary to this decrease, HC and CO emissions of all mixtures (except DBu5) increased due to the flame-quenching effect caused by the high alcohol mixture ratio. When CO emissions are compared with diesel, DPro35, DBu35 and DPen35 blends increased by 79.68%, 66.01% and 93.35%, respectively.

- The cooling effect of the LHE and -OH groups on alcohols suppressed the PAH formation caused by diesel fuel and reduced total PAH emissions. DPro and DBu mixtures performed better than DPen mixtures in reducing the PAH concentration in the exhaust gas. The reduction amounts of binary blends are DPro (71.20%) > DBu (66.86%) > DPen (0.59%) at 5% blends, and DBu (80.98%) > DPro (61.50%) > DPen (42.02%) at 35% blends.
- Differences were observed between alcohol mixtures in the distribution of PAH emissions according to the number of rings. The highest ratios in the distribution of two-ring aromatics were determined in DBu5, DBu20 and DBu35 blends. Five-ring aromatics were not detected in the blends of DPro5, DPro20, DPen20 and DPen35. A minimal occurrence of higher ring PAHs prevents total PAH formation, which can cause wet stacking.
- There was a decrease in the toxicities of all binary mixtures (except DPen5) depending on the alcohol blend ratio. The order of the maximum reduction in toxicity in the 20% mixtures is DPro (91.23%) > DBu (87.53%) > DPen (64.49%). In the mixture ratio of 35%, this order was determined as DPen (84.34%) > DPro (75.81%) > DBu (67.29%). The presence of high-ring aromatics in the PAH distribution of the blends directly affected the toxicity.

Overall, all alcohol types showed similar characteristics in terms of reducing NO_x and PAH emissions, with benefits for the environment, human health and engine endurance. However, in order to evaluate regulated emissions together with PAH formation mechanisms, it is recommended to carry out long-term tests of these alcohol types in other engine types and test conditions.

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