

## Article

# Comparative Assessment of Polycyclic Aromatic Hydrocarbons and Toxicity in a Diesel Engine Powered by Diesel and Biodiesel Blends with High Concentrations of Alcohols

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**Abstract:** Higher carbon alcohols such as *n*-propanol, *n*-butanol, and *n*-pentanol that can be produced from biomass can be used as alternative fuels in diesel engines. These alcohols can mix with both diesel fuel and biodiesel without any phase separation. Currently, unregulated emissions such as toxicity and total polycyclic aromatic hydrocarbon (PAH) from the use of these alcohols are not monitored. Investigating the effects of increasing the alternative fuel concentration for use in a diesel engine on PAH emissions will contribute to the protection of the environment and extend the engine's operating life. In this study, the effects of adding 35% (by volume) *n*-propanol, *n*-butanol and *n*-pentanol to diesel and biodiesel on unregulated emissions in a diesel engine were compared. In the total PAH emission of biodiesel, the mixture containing *n*-pentanol stood out compared to other mixtures with a decrease of 39.17%. In higher alcohol-diesel mixtures, the highest reduction was observed in the *n*-butanol mixture as 80.98%. With respect to toxic emissions, very close values were obtained in biodiesel blends up to 94.15%, although *n*-butanol showed a maximum reduction of 84.33% in diesel blends. All these reductions also prevented the formation of high-cycle PAHs. The results obtained showed that the use of high carbon alcohols in a high mixing ratio contributed to the improvement of the fuel properties of biodiesel and to an increase in the alternative fuel mixing ratio with the reduction of PAH emissions from diesel fuel.

**Keywords:** diesel fuel; biodiesel; mixing ratio; higher alcohol; toxicity; total PAHs



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## 1. Introduction

Despite the introduction of electric vehicles to the market, the fact that diesel engines are still used in electricity generation shows that the need for diesel fuel will continue. Since it will not be possible to meet the increasing fuel need solely from limited oil resources, alternative fuels must be used [1,2]. At the same time, reducing the pollutants emitted from diesel combustion has become a mandate for the sake of the environment and human health. In many years of research, biodiesel and alcohol have been suitable alternative fuels for diesel engines [3,4]. Since alcohols have a low cetane number, they cannot be used directly in diesel engines. However, it can be used by mixing with diesel fuel in certain ratios [4]. Biodiesel is a sustainable alternative fuel for diesel engines and is of great importance for the future of diesel engines. Due to the fuel properties of biodiesel, using it directly in diesel engines for long durations can cause serious damage to the engine. In addition, it is important for biodiesel to maintain phase stability under operating conditions at low temperatures [4,5]. In order to prevent such problems and increase adoption of biodiesel, the fuel properties of biodiesel must be improved. According to literature, adding alcohol to biodiesel at certain rates improves the fuel properties of biodiesel and reduces its emissions [6–8]. Among the alcohols, methanol and ethanol are the most tested

alcohols for this purpose. However, in recent studies, the use of high-carbon alcohols such as *n*-propanol, *n*-butanol, and *n*-pentanol, which can be produced from biomass and have better fuel properties than low-carbon alcohols, has become widespread. In addition, such research is aimed at reducing emissions by mixing these alcohols with diesel fuel [9–11]. In the studies on the use of those alcohols with both biodiesel and diesel fuel, the levels of regulated emissions such as hydrocarbon (HC), carbon monoxide (CO) and nitrogen oxide (NO<sub>x</sub>) were investigated [12].

In addition to the regulated emissions, it is very important to detect PAH emissions, which are not subject to any regulation but have a carcinogenic effect on human health. Additionally, PAHs have been identified as carcinogens by both the International Agency for Research on Cancer (IARC) and the US Environmental Protection Agency (EPA) [13,14]. PAH emissions also cause technical problems such as wet stacking, which negatively affects the operation of the diesel engine [15]. For these reasons, PAHs must be detected and strictly controlled. However, there are very few studies in the current literature investigating the PAH emissions of diesel or biodiesel. From the available literature, PAH formation has been associated with cold burning as a result of low load operation. The evaluation of bio-based, long-chain, ether-oxygen additives in terms of regulated and unregulated emissions in a diesel engine was performed by Wu et al. [16]. The addition of bio-based, long-chain ethers reduced particulate PAH emissions by 39–67%, gaseous PAH emissions by 25–44%, and PAH toxicity by 32–55%. Correa and Arbilla [17] conducted PAH emission tests with a heavy-duty diesel engine fed with pure diesel and diesel/biodiesel blends. The authors reported PAH reduction when biodiesel was added to diesel. Yilmaz and Davis investigated PAH formation in a diesel engine operating with diesel, biodiesel and biodiesel/*n*-butanol mixtures [18]. PAH emissions for biodiesel and blended fuels were found to be significantly lower as compared to diesel fuel. In these studies, the effects of high-carbon alcohols such as *n*-propanol, *n*-butanol, and *n*-pentanol on PAH emissions were lacking.

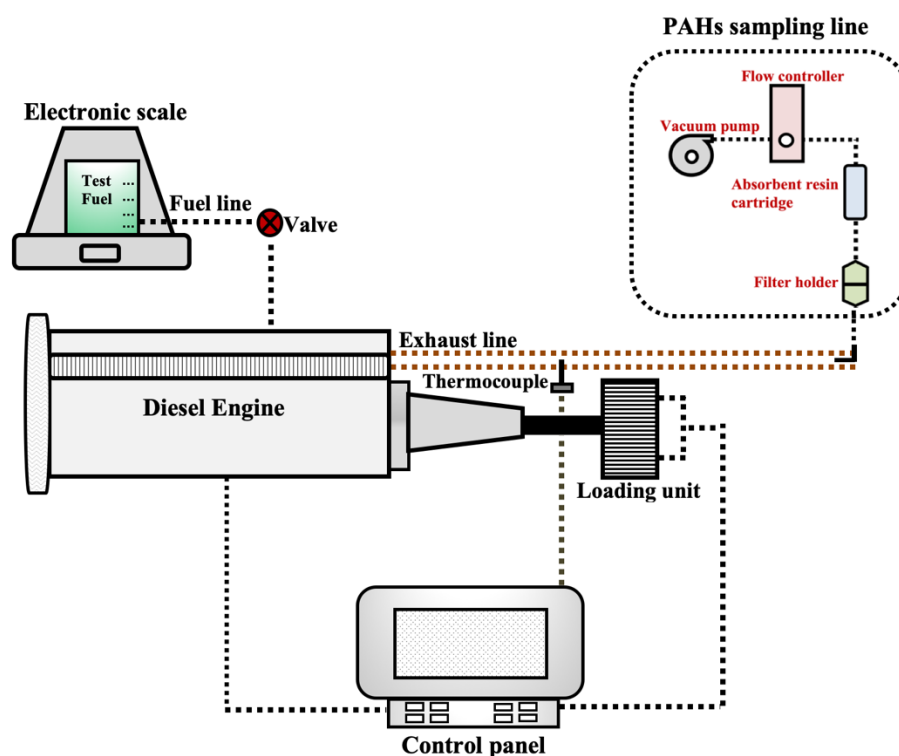
The use of these alcohols, which will be of great importance in the future, together with biodiesel and diesel in high mixing ratios, will have positive contributions to the environment and economic development. It has been stated in the literature that alcohols can be used in diesel engines with up to a 40% mixing ratio [7,10]. However, this ratio could not be reached efficiently in studies conducted with low-carbon alcohols.

In order to fill this gap in the literature and to ensure that high carbon alcohols reach a high mixing ratio in the blends, this study aims to examine the effects of 35% mixing ratio of alcohols on PAH emissions. For this purpose, the effects of biodiesel and diesel mixtures containing 35% (by volume) *n*-propanol, *n*-butanol, and *n*-pentanol on total PAH emission, PAH distribution, and PAH toxicity were determined and compared with those of diesel fuel.

## 2. Experimental Setup

### 2.1. Test Engine and Fuels

The schematic of the experimental system employed in this study is shown in Figure 1. Experiments were carried out on a four-cylinder, naturally aspirated, four-stroke, indirect-injection ONAN DJC diesel engine.



**Figure 1.** Experimental setup and PAH Sampling.

The main specifications of the engine are shown in Table 1. The fuels used in this work include diesel, methyl esters of waste cooking oil as biodiesel, *n*-propanol (99.8%, anhydrous), *n*-butanol (99.8%, anhydrous), and *n*-pentanol (99%, anhydrous). Ultra-low-sulfur highway diesel was purchased from Valero. *n*-Propanol (CAS No: 71-23-8), *n*-butanol (CAS No: 71-36-3), and *n*-pentanol (CAS No: 71-41-0) were obtained from Univar Chemistry. The waste oil methyl ester used in this study was produced from waste cooking oil collected from restaurants. The conversion of waste cooking oil into biodiesel was performed through three stage transesterification using acid catalysis. The composition of biodiesel mainly depends on its feedstock. In order to identify the composition of biodiesel used in this study, the fatty acid composition of the waste oil biodiesel was tested using the EN 15779 method, utilizing an Agilent Technologies 6890 Network Gas Chromatograph system. The gas chromatograph column used was DB-225 (30 m long, 0.25 mm diameter and 0.2  $\mu$ m film thickness). Analysis of the waste cooking oil biodiesel showed that it consisted of 81.4% unsaturated fatty acid methyl esters (FAME) and 13.28% saturated FAMEs. The six kinds of blended fuels were prepared by the volume proportion of 35% of each alcohol in diesel and biodiesel, and are identified as BPro35, BBu35, and BPen35 for the biodiesel blends and DPro35, DBu35, and DPen35 for the diesel blends, respectively. Pure diesel fuel and biodiesel are identified as D100 and B100, respectively. The waste cooking oil biodiesel and blended fuels properties were tested using ASTM test standards. The fuel properties tests were performed in a laboratory under controlled temperatures and humidity to ensure accurate results. All tests were run in triplicate. The cetane number was measured with a PAC-Herzog Cetane ID 510 instrument (PAC L.P., Houston, TX, USA) according to ASTM D613. ViscoLab 4000 (PAC L.P., Houston, TX, USA) was used to determine the kinematic viscosity correlates with ASTM D445. The measurement was performed at 40 °C. The heating value was measured by a Parr 6400 Automatic Isoperibol Calorimeter (Parr Instrument, Moline, IL, USA) according to ASTM D240. The density was determined using VIDA 40 Density (Light to Heavy) (PAC L.P., Houston, TX, USA), in compliance with ASTM D-4052 standard methods. Flash Point was tested using HFP 380 s Semi-Automatic Flash Point Testers (PAC L.P., Houston, TX, USA) according to ASTM D93-94. Cold filter plugging point (CFPP) was determined following ASTM D6371, utilizing a PAC-ISL-OptiFPP model

analyzer (PAC L.P., Houston, TX, USA). The major properties of each fuel sample are given in Table 2.

**Table 1.** Technical specifications of test engine.

| Engine Type                     | Onan DJC            |
|---------------------------------|---------------------|
| Intake system                   | Naturally aspirated |
| Fuel injection system           | Indirect            |
| Stroke (mm)                     | 92.08               |
| Bore (mm)                       | 82.55               |
| Displacement (cm <sup>3</sup> ) | 1970                |
| Number of cylinders             | 4                   |
| Number of cycles                | 4 cycle             |
| Compression ratio               | 19:1                |
| Max output (kW)                 | 12                  |
| Max speed (rpm)                 | 1800                |
| Injection pressure (MPa)        | 13.1                |
| Injection timing (bTDC)         | 18 °CA              |

**Table 2.** Test fuels specifications.

| Items              | Density (g/mL) | Lower Heating Value (MJ/kg) | Cetane Number | Kinematic Viscosity at 40 °C (mm <sup>2</sup> /s) | Flash Point (°C) | Cloud Point (°C) | CFPP (°C) |
|--------------------|----------------|-----------------------------|---------------|---------------------------------------------------|------------------|------------------|-----------|
| Diesel             | 0.818          | 44.8                        | 54            | 2.95                                              | 74               | −12              | −21       |
| Biodiesel          | 0.855          | 40.5                        | 52            | 4.57                                              | 126              | −8.1             | −13.2     |
| <i>n</i> -Propanol | 0.803          | 30.63                       | 12            | 1.74                                              | 22               | -                | <−51      |
| <i>n</i> -Butanol  | 0.810          | 33.10                       | 17            | 2.23                                              | 35               | -                | <−51      |
| <i>n</i> -pentanol | 0.815          | 34.94                       | 20            | 2.89                                              | 49               | -                | −40       |
| BPro35             | 0.836          | 30.91                       | 40.20         | 3.51                                              | 91.8             | −13.4            | −19.5     |
| BBu35              | 0.840          | 38.67                       | 41.85         | 3.72                                              | 92.3             | −13.88           | −19.9     |
| BPen35             | 0.842          | 38.72                       | 42.72         | 3.86                                              | 94.1             | −12.6            | −18.4     |
| 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       |

It should be noted that higher alcohol concentrations in the mixtures reduce the density, kinematic viscosity, and cetane number as shown in Table 2. Fuel properties of binary mixtures comply with ASTM standards and no phase separation was observed. Their cold flow properties are at a level that will enable operation at low temperatures.

## 2.2. PAH Sampling and Testing

The engine initially remained in operation with diesel for ten minutes to minimize the cold start effect before collecting the PAH sample for each fuel blend. Test engine PAH emissions sample collection and analysis were determined for test fuels according to EN ISO 11338-2:2003 test standard. PAH samples were collected for three hours while the engine was run at idle on each fuel and the procedure was repeated three times for greater experimental assurance. A sequence of collection media was used to gather PAHs from the undiluted exhaust sample which was received at 10 L per minute (l/min). As shown in Figure 1, aromatic hydrocarbons were gathered in an adsorbent resin cartridge (Sigma Aldrich, St. Louis, MO, USA), which was filled with two-stage Amberlite XAD-2 adsorbent resin. The temperature throughout the filter was controlled so that it did not exceed 50 °C on average. A 5 mL of HPLC grade hexane was used for separate extractions of the cartridge and the filter. The extracts were removed from a purification column filled with alumina and Na<sub>2</sub>SO<sub>4</sub> and activated at 120 °C for twenty-four hours before further use. PAHs were recovered with 50/50 vol% HPLC-grade benzene/acetonitrile and concentrated using

nitrogen blowdown. The solutions were kept at  $-80\text{ }^{\circ}\text{C}$  until the next analysis step. Helium was used as a carrier gas. The Gas Chromatography-Mass Spectrometry (GC-MS) system was utilized to detect and quantify PAHs following a Selected Ion Monitoring (SIM) process. The GC-MS system specifications are shown in Table 3. The accuracy and precision of the optimized analytical method were determined by using a Standard Reference Material (SRM) 2975 and an exhaust gas sample spiked with all PAHs. To confirm that the method is suitable for its intended use, a validation process was carried out by establishing the basic analytical requirements of the performance to be appropriate for the quantitation of PAHs in exhaust samples. Reproducibility was evaluated at the same concentration level, and spiked samples were analyzed three times.

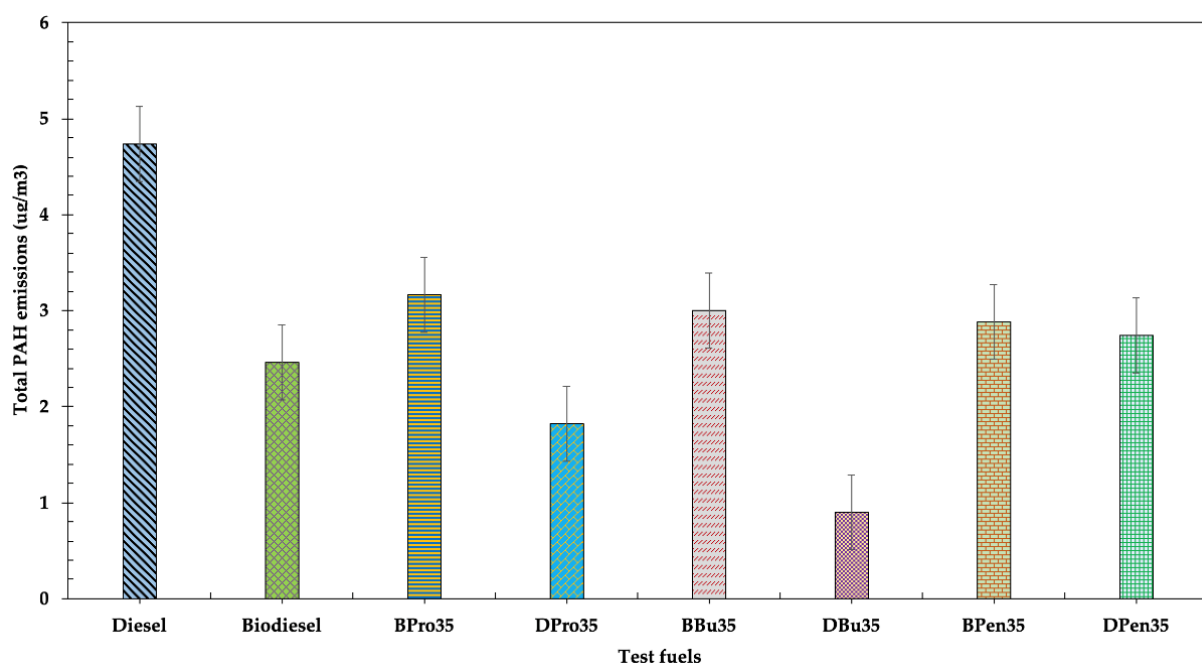
**Table 3.** Thermal Program GC-MS.

| Instrument Details    | GC-MS: HP 5890/5971A<br>Column: DB5-MS                                                                                                                                                                                                                         |
|-----------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Injection Volume      | 1 $\mu\text{L}$                                                                                                                                                                                                                                                |
| Injection Temperature | 300 $^{\circ}\text{C}$                                                                                                                                                                                                                                         |
| Thermal Program       | Hold 70 $^{\circ}$ for 1 min<br>Heat from 70–200 $^{\circ}\text{C}$ @ 70 $^{\circ}\text{C}/\text{min}$<br>Hold 200 $^{\circ}\text{C}$ for 2 min<br>Heat 200–300 $^{\circ}\text{C}$ @ 7 $^{\circ}\text{C}/\text{min}$<br>Hold 200 $^{\circ}\text{C}$ for 10 min |

### 3. Results and Discussions

#### 3.1. PAH Concentration in the Exhaust

The total PAH emission concentration ( $\mu\text{g}/\text{m}^3$ ) in the exhaust gas is given in Figure 2 and the total PAH concentrations are tabulated in Table 4.



**Figure 2.** PAH Concentration in the exhaust.

Table 4. PAH concentration in exhaust.

| PAH                  | Number of Rings | Total PAHs ( $\mu\text{g}/\text{m}^3$ ) |           |        |        |        |        |        |        |
|----------------------|-----------------|-----------------------------------------|-----------|--------|--------|--------|--------|--------|--------|
|                      |                 | Diesel                                  | Biodiesel | BPro35 | BBu35  | BPen35 | DPro35 | DBu35  | DPen35 |
| Naphthalene          | 2               | 1.93                                    | 0.76      | 2.21   | 1.88   | 1.82   | 0.52   | 0.23   | 0.81   |
| Acenaphthylene       | 2               | 0.21                                    | 0.25      | 0.30   | 0.93   | 0.90   | 0.37   | 0.33   | 0.42   |
| Fluorene             | 2               | 0.59                                    | 0.22      | 0.23   | 0.14   | 0.12   | 0.59   | 0.22   | 0.96   |
| Phenanthrene         | 3               | 1.19                                    | 0.66      | 0.23   | 0.02   | 0.02   | 0.23   | 0.02   | 0.43   |
| Fluoranthene         | 3               | 0.29                                    | 0.18      | 0.07   | 0.00 * | 0.00 * | 0.05   | 0.04   | 0.06   |
| Pyrene               | 4               | 0.40                                    | 0.31      | 0.09   | 0.01   | 0.01   | 0.05   | 0.04   | 0.05   |
| Benzo[a]anthracene   | 4               | 0.00 *                                  | 0.01      | 0.00 * | 0.00 * | 0.00 * | 0.00 * | 0.00 * | 0.00 * |
| Chrysene             | 4               | 0.09                                    | 0.07      | 0.02   | 0.01   | 0.01   | 0.01   | 0.01   | 0.00 * |
| Benzo[k]fluoranthene | 4               | 0.00 *                                  | 0.01      | 0.00 * | 0.00 * | 0.00 * | 0.00 * | 0.00 * | 0.00 * |
| Benzo[a]pyrene       | 5               | 0.01                                    | 0.00 *    | 0.00 * | 0.00 * | 0.00 * | 0.00 * | 0.00 * | 0.00 * |

\* undetected.

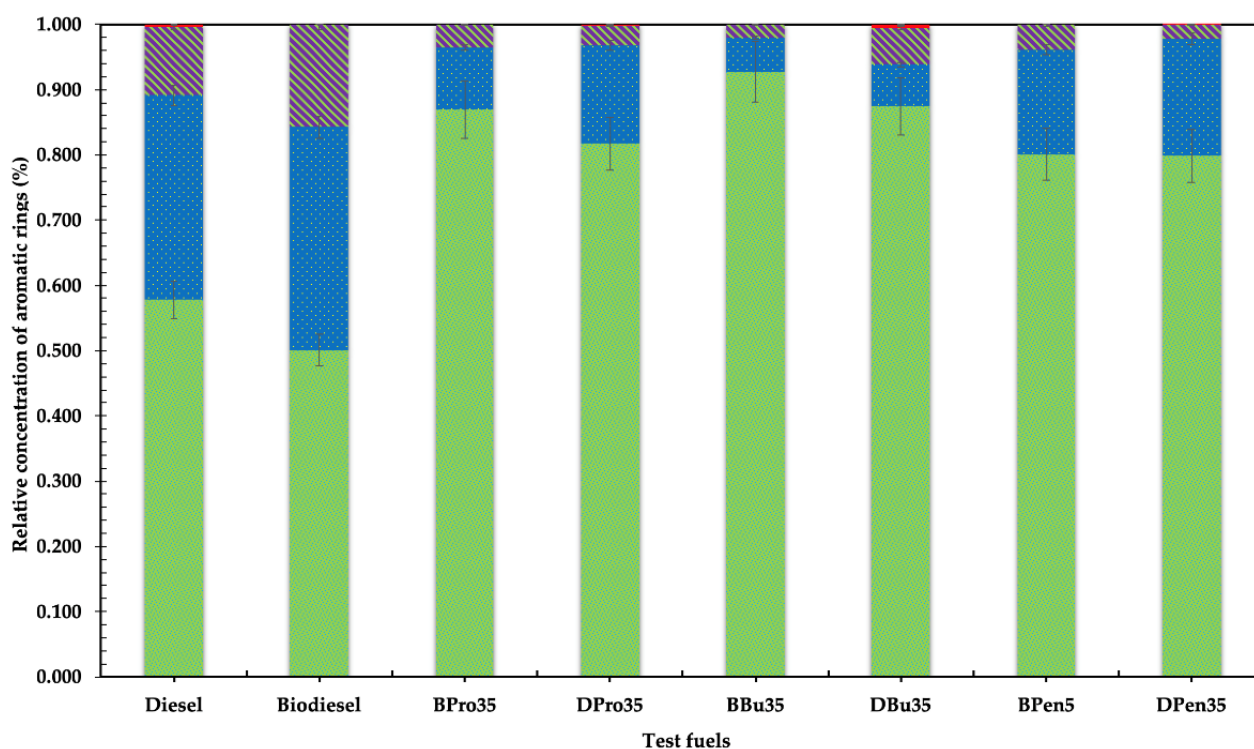
When Figure 2 is viewed in terms of diesel, it is clearly seen that it emits significantly higher PAH emissions compared to the binary blends. The total PAH concentration of diesel fuel, mostly naphthalene (two-ring) and phenanthrene (three-ring) was obtained as  $4.73 \mu\text{g}/\text{m}^3$ . When *n*-propanol, *n*-butanol, and *n*-pentanol were added to the biodiesel and diesel fuel, significant reductions were obtained in the total PAH emission of all blends. The order of this reduction is DBu35 (80.98%) > DPro35 (61.50%) > DPen35 (42.02%) > BPen35 (39.17%) > BBu35 (36.65%) > BPro35 (36.20%) compared to diesel. With the addition of 35% alcohol to the diesel fuel and biodiesel, PAH emissions were detected below the Occupational Safety and Health Administration's (OSHA)-Permissible Exposure Level (PEL:  $0.2 \text{ mg}/\text{m}^3$ ). It has been determined that the addition of alcohol at a high mixing ratio will be effective in reducing the total PAH emission concentration. This situation will also have the effect of increasing the durability of the diesel engine and its potential to prevent wet stacking [15,19].

The maximum reduction among alcohols was obtained in the diesel-*n*-butanol mixture. Thus, the use of *n*-butanol at a high mixing ratio (up to 35%) with diesel helps to reduce the total PAH emission.

### 3.2. Distribution of PAHs

In addition to the amount of PAH formation in the exhaust gas, the distribution of PAH should also be detected. The number of aromatic rings and the relative distribution of PAHs of the test fuels are shown in Figure 3.

According to Figure 3 and Table 4, it is seen that the PAH distribution of all test fuels is higher in the two- and three-ring aromatic components. While 5-ring aromatics were not detected in biodiesel alcohol blends, they were detected in DPen35 (0.22%), DBu35 (0.5%) and DPro35 (0.1%) blends. High levels of low-rings PAHs may be due to the amount of the blended fuels pyrolyzed from incomplete combustion due to the addition of alcohol [20,21]. Additionally, the reason for the formation of five-ring aromatics can be attributed to the ignition delay of alcohols in this ratio depending on the cetane number and the inability of alcohol radicals to suppress the formation of five-ring aromatics in the final stage of combustion. Minimizing PAHs with higher rings in the PAH distribution will prevent total PAH formation that could cause diesel engine failure such as wet stacking [22]. Thus, the blended fuels without 5-ring aromatic compounds minimized the production of higher PAHs, making the blended fuels superior to diesel in terms of possible engine failures and pollutions.



**Figure 3.** Relative Distribution of PAHs.

### 3.3. Toxicity of PAH Emissions

Toxicity is defined as the toxic effects of a substance that result in death or serious damage after exposure or contamination to that substance. This definition is used to specify toxic equivalence factors (TEFs). The total carcinogenicity of PAHs is defined as TEFs values, and the weighted benzo[a]pyrene equivalent (BaPeq) of each PAH compound was calculated based on TEF [23–25]. The use of TEFs allows the concentration of PAHs to be converted to equipotent concentrations of BaPeq as given Equation (1).

$$\text{BaPeq} = \sum \rho_i \times \text{TEF}_i \quad (1)$$

where  $\rho_i$  is the volume concentration of each PAHs in the exhaust ( $\text{ng}/\text{m}^3$ ) and  $\text{TEF}_i$  is the toxicity equivalent factor of the individual PAHs.

The toxicity distribution of PAH emissions is shown in Figure 4 and toxicity BaPeq concentration in the exhaust is given in Table 5. When the toxicities of 35% blends are compared with diesel fuel, a decrease of 94.15%, 91.78%, 91.47%, 75.81%, 67.28%, and 84.33% was observed in BPro35, BBu35, BPen35, DPro35, DBu35, and DPen35, respectively.

These reductions are due to the very low PAH level affecting BaPeq in high alcohol mixtures of 35% and the chemical composition of the mixtures. The best reduction performance was obtained from butanol blends. In general, alcohol mixing ratio together with other fuel properties such as cetane number, density and viscosity can directly affect the amount of high molecular PAHs that will be formed at the end of combustion [26–29]. All these factors directly contributed to the amount of toxicity reduction among the mixtures [30]. As a result, although all six blends reduce toxicity compared to diesel, the negative effects of other fuel properties on emissions should not be ignored due to the increased alcohol blend ratio.

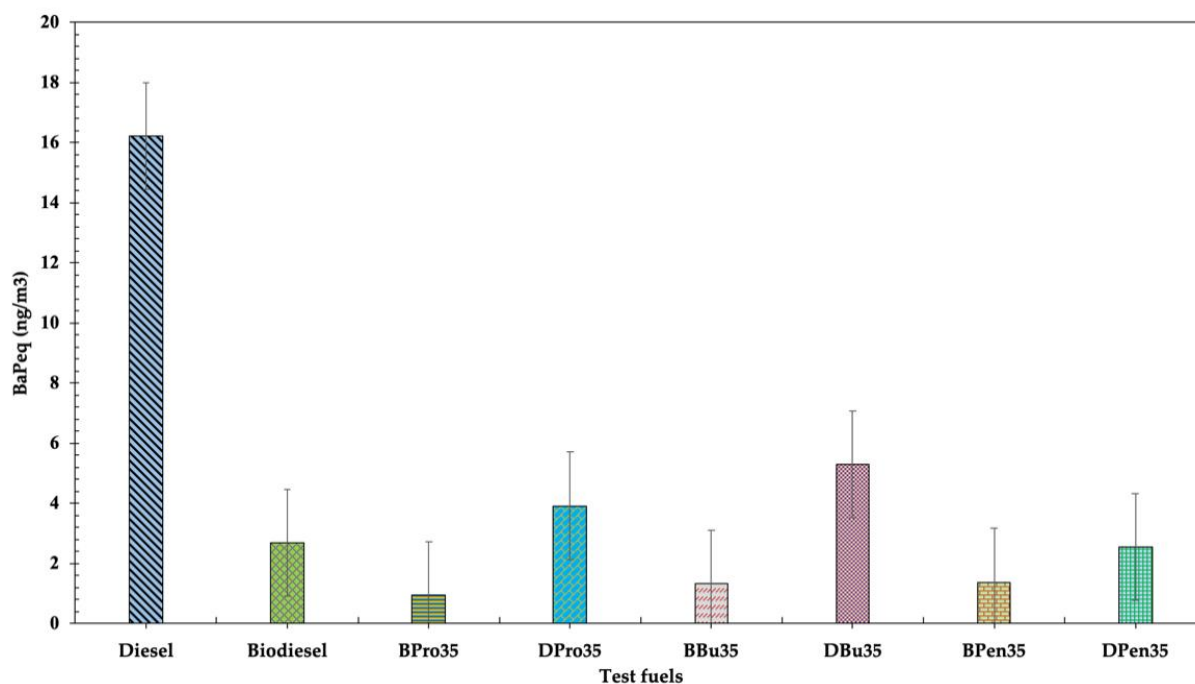


Figure 4. Toxicity of PAH emissions.

Table 5. Toxicity BaPeq concentration in exhaust.

| PAH                  | Number of Rings | Toxicity BaPeq (ng/m <sup>3</sup> ) |           |        |       |        |        |       |        |
|----------------------|-----------------|-------------------------------------|-----------|--------|-------|--------|--------|-------|--------|
|                      |                 | Diesel                              | Biodiesel | BPro35 | BBu35 | BPen35 | DPro35 | DBu35 | DPen35 |
| Acenaphthylene       | 2               | 0.211                               | 0.246     | 0.301  | 0.953 | 1.00   | 0.373  | 0.330 | 0.416  |
| Fluorene             | 2               | 0.593                               | 0.223     | 0.234  | 0.219 | 0.20   | 0.594  | 0.225 | 0.964  |
| Phenanthrene         | 3               | 1.194                               | 0.660     | 0.225  | 0.062 | 0.06   | 0.227  | 0.022 | 0.431  |
| Fluoranthene         | 3               | 0.288                               | 0.180     | 0.075  | 0.079 | 0.10   | 0.049  | 0.036 | 0.061  |
| Pyrene               | 4               | 0.403                               | 0.305     | 0.095  | 0.010 | 0.01   | 0.049  | 0.045 | 0.053  |
| Benzo[a]anthracene   | 4               | 0.000                               | 0.919     | 0.000  | 0.000 | 0.00   | 0.000  | 0.000 | 0.000  |
| Chrysene             | 4               | 0.094                               | 0.065     | 0.018  | 0.009 | 0.01   | 0.005  | 0.005 | 0.005  |
| Benzo[k]fluoranthene | 4               | 0.046                               | 0.077     | 0.000  | 0.000 | 0.00   | 0.053  | 0.000 | 0.107  |
| Benzo[a]pyrene       | 5               | 13.378                              | 0.000     | 0.000  | 0.000 | 0.00   | 0.008  | 0.000 | 0.016  |

#### 4. Conclusions

*n*-Propanol, *n*-butanol, and *n*-pentanol can be mixed with biodiesel and diesel fuel without phase separation. The high percentage of alcohol used in the fuel composition has the potential to support the use of alternative fuels in diesel engines. In order to strengthen this support, it is necessary to know the effects of the mixtures on the environment. However, the PAH emissions of mixtures containing high alcohol content have not been investigated in the studies carried out so far. In this study, conducted with this motivation, the effects of biodiesel and diesel mixtures containing 35% *n*-propanol, *n*-butanol, and *n*-pentanol on PAH emissions were compared.

According to the purpose of the study, the following conclusions can be drawn:

- \* The addition of 35% alcohol improved the cold flow properties, which is an important parameter for the mixtures to work at low temperatures.
- \* The significant reductions were obtained in the total PAH emission of all blends. The order of this reduction is DBu35 (80.98%) > DPro35 (61.50%) > DPen35(42.02%) > BPen35(39.17%) > BBu35(36.65%) > BPro35(36.20%) compared to diesel.
- \* While 5-ring aromatics were not detected in biodiesel alcohol blends, they were detected in DPen35 (0.22%), DBu35 (0.5%) and DPro35 (0.1%) blends.

- \* Compared to diesel fuel, the toxicity of BPro35, BBu35, BPen35, DPro35, DBu35, and DPen35 are reduced by 94.15%, 91.78%, 91.47%, 75.81%, 67.28%, and 84.33%, respectively.

The reduction in PAH emissions by using alcohol at a high mixing ratio of 35% will have positive effects on the engine's operating performance and the environment. In order to investigate this effect in detail, it is recommended to carry out long-term tests on engines with different engine technologies.

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