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An Experimental Investigation of Unregulated Pollutants from a Multi-Cylinder Diesel Engine: Impact of Ethanol Blending on Aldehyde Emissions

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ABSTRACT

To combat global warming and reduce dependence on fossil fuels, significant efforts are being made to explore alternative/blended fuels. Usage of ethanol with fossil fuels is an effective way to mitigate regulated exhaust emissions like CO, NOx and PM. The use of alcohol-blended diesel fuel releases unregulated pollutants like formaldehyde and acetaldehyde, which, though emitted in smaller quantities, can adversely affect human health. In this investigation, a multi-cylinder in-use diesel engine was subjected to an ISO 8178 C1 (8-mode) test cycle for unregulated emissions with D20 ethanol blended diesel fuel (20% ethanol in diesel) and base diesel (D0). The primary objective was to assess the variations in the emission constituents resulting from the use of ethanol-blended fuel, compared to conventional diesel. This study aims to address the gap in the existing literature by providing a systematic methodology for collecting, analyzing, and characterizing unregulated exhaust emissions to frame future regulatory measures. Primary results indicate that the formaldehyde and acetaldehyde emissions increased by 115.51% and 3293.65%, respectively, whereas acetone emissions were reduced by 88.84% for D20 fuel over D0. Analysis of Variance (ANOVA) based statistical tool was used for finding the statistical significance of the results, which showed that the Gross Calorific Value of the fuel has the most significant impact (among Cetane Number, Flash Point, and Gross Calorific Value) on the formation of formaldehyde, acetaldehyde, acetone, and acrolein. The findings offer valuable insights into the impact of diesel-ethanol blends on emissions, enhancing understanding of alternative fuels' effects on engine exhaust composition.

1. INTRODUCTION

Diesel engines have inherent unique characteristics such as high-power density, thermal efficiency, high torque, low-end power, excellent dependability, durability, ruggedness and low fuel consumption. These characteristics makes them well-suited for off-road applications, transportation, generator set applications. However, nowadays stringent emission norms and depletion in fossil fuel reserves necessitate exploration of suitable fuel substitutes. One of the effective ways of finding substitute for these fossil fuels (such as diesel and gasoline) is blending. For instance, gasoline fuel is being blended with ethanol. The average level of ethanol blending with gasoline in India is currently at 15% and it has been mandated to increase it to 20% by the year of 2025. There is a bright possibility of using even higher blends than E20 in the future with regards to flex fuel vehicles. However, blending ethanol with diesel is not explored commercially due to various reasons such as blend separation, lower lubricity, lower cetane number, lower calorific value and more. These drawbacks can be mitigated by judicious use of suitable additives which help to improve the required diesel-ethanol blend properties. Figure 1 shows different vehicles registered fuel-wise in India and Figure 2 shows the percentage of vehicles registered category-wise [1]. From both of these figures, it is evident that gasoline and diesel still lead the market demand in India.

Usage of ethanol blended diesel has been shown to reduce emissions of regulated pollutants such as CO, PM and NOx [2]. However, the amounts of unregulated emissions with ethanol blended diesel fuel require extensive investigations [3]. Therefore, the present study aims to investigate and characterize the unregulated emissions from a D20 ethanol blend fueled diesel engine and compare with pure diesel emissions.

In recent years, there has been a growing interest in understanding the environmental impact of engine emissions, particularly those arising from the use of alternative fuels such as diesel-ethanol blends. However, despite the increasing focus on alternate fuel options, there is still a limited amount of data available on the precise quantification of unregulated pollutants, as well as on the accuracy and effectiveness of existing measurement methodologies. Unregulated pollutants, which include a variety of harmful chemical species not typically monitored by current emission standards, can significantly affect air quality and public health. Therefore, a more detailed analysis of these pollutants is essential for a comprehensive evaluation of alternative fuels' environmental impact.

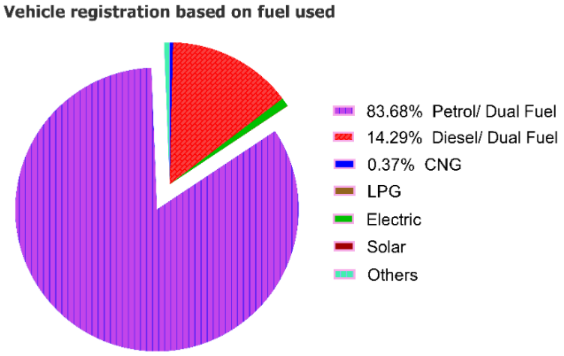

Figure 1. Vehicle registrations (fuel-wise), till 4th Jan 24
Source: Vahan Parivahan [1]

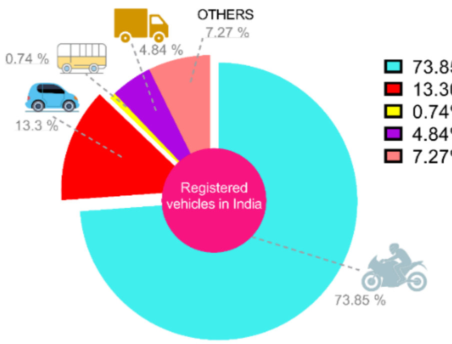

Figure 2. Registered vehicles in India
Source: Vahan Parivahan [1]

This study addresses this gap by adopting a relatively simple and accurate methodology for the collection of unregulated pollutant samples, distinguishing itself from the more complex and cumbersome techniques commonly employed in the existing literature. The chosen approach aims to improve the efficiency and reliability of data collection during engine testing, thereby providing a more accessible and effective means of analyzing emissions. The research further investigates the nature and composition of unregulated emissions generated when an internal combustion engine is fuelled with a diesel-ethanol blend, specifically D20 fuel (a blend containing 20% ethanol and 80% diesel by volume). The study places a particular emphasis on the characterization and quantification of individual unregulated species, which are often overlooked in conventional emission studies. By providing insights into the variations in emission constituents and the behaviour of these pollutants, the study contributes to a better understanding of the environmental implications of using diesel-ethanol blends as an alternative fuel. Additionally, the findings may inform future emission control strategies and regulatory measures aimed at reducing the impact of harmful engine exhaust components. Following are the problem statement and objectives for the current research study.

Problem Statement:

To investigate and characterize un-regulated emissions from multi-cylinder ethanol blended diesel engine.

Objectives:

1. To provide a systematic and step-by-step procedure for the collection, analysis, and characterization of unregulated pollutants;
2. To characterize the unregulated emission emitted from the internal combustion engine fuelled with alcohol-blended fuel;
3. To analyze the variations in the un-regulated emission constituents resulting from the use of blended fuel, compared to conventional diesel;
4. To suggest mitigation strategies for the reduction of unregulated emissions.

Research Scope:

The present study included the measurement and analysis of the following unregulated emissions from a D20 ethanol-blended diesel-fuelled multi-cylinder engine used for non-road applications:

1. Formaldehyde
2. Acetaldehyde
3. Acrolein
4. Acetone
5. Propionaldehyde
6. Crotonaldehyde
7. n-Butyraldehyde
8. Benzaldehyde
9. Isovaleraldehyde
10. Valeraldehyde
11. o-Tolualdehyde
12. m-Tolualdehyde
13. p-Tolualdehyde
14. Hexanledehyde
15. 2,5-dimethylbenzaldehyde

Research Question:

The following research question was formulated for this study: What is the impact of ethanol blending on unregulated emissions from a multi-cylinder diesel engine?

The subsequent section gives details of the different types of unregulated pollutants emitted by internal combustion engines.

2. UN-REGULATED EMISSIONS

Unregulated gaseous exhaust emissions include substances that are poisonous, carcinogenic, or act as precursors to secondary pollutants including the creation of ozone and secondary organic aerosols (SOA). Currently, unregulated emissions are not subject to government legislations. However, as the percentage of blending is increased, an increase in emissions of carbonyl compounds is expected. There are 15 such carbonyl compounds which are categorically designated as un-regulated emissions, and are listed in Table 1.

Of these, formaldehyde and acetaldehyde are particularly harmful substances. Formaldehyde has been classified as "carcinogenic to humans" by the International Agency for Research on Cancer (IARC), while acetaldehyde is classified as a possible human carcinogen (group 2B) by the same agency. Formaldehyde is absorbed through the skin and ingestion can lead to corrosive injuries in the gastrointestinal tract. On the other hand, acetaldehyde can cause dermatitis upon skin contact and has detrimental effects on the central nervous system when inhaled [4].

Table 1. List of carbonyl compounds [5]

Sr. No.	Chemical Names	Chemical Formulae	Molecular Weights (g/mole)
1	Formaldehyde	CH_2O	30.0260
2	Acetaldehyde	C_2H_4O or $CH_3CH=O$	44.0526
3	Acrolein	C_3H_4O	56.0633
4	Acetone	C_3H_6O	58.0791
5	Propionaldehyde	CH_3CH_2CHO	58.0791
6	Crotonaldehyde	C_4H_6O	70.091
7	n-Butyraldehyde	C_4H_8O	72.107
8	Benzaldehyde	C_7H_6O	106.1219
9	Isovaleraldehyde	$C_5H_{10}O$	86.1323
10	Valeraldehyde	$C_5H_{10}O$	86.1323
11	o-Tolualdehyde	C_8H_8O	120.1485
12	m-Tolualdehyde	$CH_3C_6H_4CHO$	120.15
13	p-Tolualdehyde	$CH_3C_6H_4CHO$	120.15
14	Hexanledehyde	$C_6H_{12}O$	100.1589
15	2,5-dimethylbenzaldehyde	$C_9H_{10}O$	134.1751

3. LITERATURE REVIEW

Research literatures report that as ethanol percentage rise in blended fuels, carbonyl compound emissions increase due to incomplete ethanol combustion. Jin et al. [6] conducted a study on vehicle exhaust, which included Federal Test Procedures (FTP-75) to measure unregulated emissions from E20 fuels. The authors found that on one hand the controlled emissions like carbon monoxide and hydrocarbons decreased, on the other hand the formaldehyde emissions were only half as high as acetaldehyde emissions. They also reported that as ethanol percentage increased, carbonyl compound emissions rose quickly due to incomplete ethanol combustion.

In another work, experimental research on the combustion and uncontrolled emission characteristics of a diesel engine fuelled with conventional diesel and 85% light hydrocarbon (LHC)-diesel blends was conducted by Hanyu Chen et al. [7] at a speed of 1000 rpm and load points of 100%, 75%, and 50%. The purpose of the study was to examine how mixing LHC and diesel affects emission characteristics and combustion, particularly when there is partial load. When blending LHC with pure diesel fuel, there was a phase lag in combustion and an increase in the ignition delay time. Particular NOx and CO emissions were found to be significantly reduced; however, THC emissions were greater with LHC/diesel blends. Organosilicon compounds (OSC), aromatic compounds (AC), and non-aromatic hydrocarbons and their derivatives (NAHC) were the main unregulated pollutants found in blended fuel.

Rezgui [8] examined the effect of ethanol addition on unregulated emissions using a high pressure PLOG function, CHEMKIN II, and a zero-dimensional model (Senkin). The primary goal of this study was to understand how ethanol oxygenate affected formaldehyde, acetaldehyde, acetylene, and butadiene levels. By gradually adding 5% of ethanol to neat n-heptane/methyl-decanoate/methyl-9-decanoate fuel, blended fuels were produced. In comparison to binary diesel-biodiesel fuel, ethanol blends have higher carbonyl levels (CHO and CHCHO). For butadiene and acetylene, the opposite pattern was noted.

Theinnoi et al. [9] examined the effects of ethanol on emissions and combustion in a single-cylinder, un-modified diesel engine. A blend of 10–50 vol% of ethanol was selected to be combined with diesel and biodiesel fuels. The authors found that low calorific content of the diesel, biodiesel, and ethanol fuel blends led to an increase in fuel consumption. Compared to diesel fuel, the engine running on relatively low ethanol proportion blends had a greater brake thermal efficiency. With an increase in ethanol amount, unburned hydrocarbons (HC), un-regulated emissions and carbon monoxide (CO) increased while NOx decreased.

To assess how ethanol blended diesel fuels affect uncontrolled emissions like acetaldehyde, CO_2, and unburned ethanol as well as controlled emissions like smoke, THC, CO, and NOx, distillation temperature, He et al. [10] examined a four-cylinder direct injection diesel engine. When compared to diesel fuel, the blends greatly reduced smoke at high loads while having a minor negative impact on CO, acetaldehyde, and unburned ethanol emissions. Because the mixture is often leaner, such blends have a small effect on reducing smoke at low loads. The authors suggested that the mixes' emissions of CO, unburned ethanol, and acetaldehyde can be somewhat reduced with the help of additives and ignition improvers.

He [11] conducted an experimental evaluation of the impacts of several ethanol-diesel blended fuels on the operation and emissions of a single cylinder engine, which is also considered in the present study. The authors tested emissions from an IC engine fuelled with a number of diesel blends with up to 20% ethanol and contrasted against emissions with pure diesel fuel. Both controlled and uncontrolled emissions were measured; wherein formaldehyde (CH_2O), formic acid (HCOOH), acetaldehyde (CH_3CHO), and ethanol (C_2H_sOH) comprised the uncontrolled emissions. The controlled emissions were composed of HC, CO, NOx, and CO2. The findings of this research study demonstrated that formaldehyde, formic acid, and acetaldehyde emissions from diesel/ethanol-fuelled engines were essentially higher than those from diesel fuel. The formaldehyde emissions were increased by 125% with 20%

Zarante [12] conducted an experiment on new off-road applications to understand the technological challenges and requirements for improved emissions performance, considering both regulated and unregulated emissions. The experiment measured emissions of various substances such as aldehydes and ketones, volatile organic compounds (VOC), elemental and organic carbon (EC/OC), polycyclic aromatic hydrocarbons (PAH), semi-volatile organic compounds (SVOC) and intermediate soluble organic compounds (IVOC). When alcohols such as ethanol undergo oxidation, aldehydes such as formaldehyde (CH_2O), acetaldehyde (C_2H_4O), propionaldehyde (CH_3CH_2CHO), and crotonaldehyde (C_4H_6O) are formed. When a 10 percent blend of ethanol with diesel (D10) was used, it was observed that aldehyde emissions increased by almost 40 percent. This increase in aldehyde emissions occurred due to the presence of the hydroxyl functional group (OH) in ethanol.

The study [13], on ethanol-diesel blends have demonstrated reductions in CO and smoke opacity, but with increased emissions of carbonyl compounds, indicating a trade-off between improved combustion and higher levels of certain unregulated pollutants. Additionally, research shows that higher ethanol content typically enhances thermal efficiency and reduces particulate emissions, but may also raise brake-specific fuel consumption due to ethanol's lower energy density.

Mohammad et al. [14] conducted research on biodiesel derived from waste cooking oil. Experimental trials were conducted at a consistent engine speed of 2250 rpm across five distinct engine loads. The results show promising reductions in HC and CO emissions, though it often results in higher brake-specific fuel consumption due to lower energy content compared to diesel. Additionally, it was concluded that blending with alcohols like butanol can further enhance emission reductions, particularly for CO and HC, while impacting NOx emissions variably across different blend ratios. However, increase in the levels of unregulated pollutants was observed.

Due to alcohols' partial oxidation during combustion, the addition of alcohols to diesel alter the combustion process and result in the creation of oxygenates such formaldehyde, acetaldehyde, and ketones. From the above-mentioned brief literature survey, it can be concluded that with the use of ethanol blended fuel, regulated pollutants such as CO, HC, VOC are reduced as compared with neat diesel, but on the other hand the amount of un-regulated emission is increased.

4. EFFECT OF ETHANOL BLENDS ON EMISSIONS

Diesel engines are known for their reliability, dependability and efficiency. Unfortunately, they are also significant sources of pollution. While it is difficult to reduce the levels of noxious combustion gases in diesel engines through improvements in the combustion chamber and fuel injection process alone, it is believed that clean combustion in diesel engines can be achieved through reformulation of the fuel constituents. One way to achieve this is by adding ethanol to diesel fuel, which changes its chemical properties. With the blend of ethanol and diesel, properties such as density, cetane number, thermal efficiency, viscosity and boiling point decrease. Table 2 shows the individual fuel properties of diesel and ethanol.

Table 3 presents the key properties of the base diesel fuel (D0) and the diesel-ethanol blend (D20). The comparison reveals some notable deviations in certain fuel characteristics when ethanol is blended with diesel. Specifically, the D20 fuel, which contains 20% ethanol and 80% diesel, exhibited slight variations in properties such as Flash Point, cetane number, water content, and gross calorific value. The Flash Point of D20 was lower than that of the base diesel, indicating a reduced temperature threshold for ignition, which is typical when ethanol is blended with diesel. The cetane number, a measure of combustion quality, also showed a marginal change, potentially influencing the ignition delay in the combustion process. Additionally, an increase in water content was observed in D20 due to the hygroscopic nature of ethanol, which can absorb moisture from the atmosphere. The gross calorific value of the D20 blend was slightly reduced compared to that of base diesel, reflecting the lower energy content of ethanol. All fuel properties were measured and evaluated according to the IS1460 test standard, ensuring that the data was obtained using reliable and standardized testing procedures. These differences in fuel properties influence the engine performance, combustion characteristics, and emissions, which underscores the importance of understanding the effects of alternative fuel blends on internal combustion engines

To ensure that ethanol-blended diesel fuel exhibits the necessary physicochemical properties for optimal engine performance and fuel stability, the additive is introduced. The additive is designed to address specific challenges associated with blending ethanol and diesel, such as phase separation, poor lubricity, low cetane number, and increased corrosion potential. Because diesel is a non-polar hydrocarbon and ethanol is a polar, hygroscopic substance, their direct mixing results in immiscibility, especially under varying temperature and humidity conditions. This leads to phase separation and stratification in the fuel, adversely affecting its consistency and performance.

Table 2. Diesel-ethanol properties

Property	Fuel	
	Diesel	**Ethanol**
Flash Point [°C]	min. 55	12.8
Lower Heating Value [MJ/kg]	43.700	26.900
Stoichiometric Air/Fuel ratio [-]	14.60	9.01
Density at 15°C [kg/m^3]	820 - 845	792
H [wt. %]	~13.92	~13.04
C [wt. %]	~85.24	~52.17
S [wt. %]	Max 0.01	0.0
O [wt. %]	~0.74	~34.78
C/H mass ratio [-]	6.12	3.97
Autoignition temperature [°C]	~315	~423
Kinematic viscosity at 40°C [mm^2/s]	2–4.5	1.13
Calorific value (KJ/ Kg)	42600	26700
Latent heat of vaporization (KJ/Kg)	700	904

Table 3. Base diesel and D20 properties

Property	UNIT	SPECS	Base Diesel (D0)	D20
Appearance	-	Clear, bright and free from sediments	Clear and bright liquid	Clear and bright liquid
Density @ 15°C	kg/m³	810-845	818.5	817.9
Kin Viscosity @ 40°C	cSt	1.9-4.5	2.32	2.501
Flash Point	°C	Min 10	42.8	10.6
Total Sulphur	mg/kg	Max 10	5.3	4.1
Cetane Number	-	Min 51	55	48.15
Lubricity Corrected Wear Scar Diameter (wsd 1.4) at 60°C	microns	Max 460	434	428
Oxidation Stability	g/m³	Max 60	32.4	31.5
Oxidation Stability by Rancidity meter	hours	Min 5	>20	5.03
Ash	% by mass	Max 0.01	0.0053	0.0035
Gross Calorific Value	Cal/g	>10875	10993	10344
Total Contamination	mg/kg	Max 24	22	15
Water Content	mg/kg	Max 300	103	398
FAME Content	% v/v	Max 7	Nil	Nil

In addition to stabilizing the blend, the additive also enhances other physicochemical properties of the fuel. For instance, a cetane improver is added to increase the cetane number, which is an indicator of the fuel's ignition quality and combustion characteristics. A lubricity enhancer is also included to mitigate the lower lubricity of ethanol, reducing wear on engine components. Anti-corrosion agent is used to counteract ethanol's tendency to absorb moisture, which can lead to corrosion in the fuel system. In this study, the additive was formulated carefully by selecting the appropriate chemicals.

However, the impact of ethanol on diesel fuel engine varies depending on engine operating conditions, ethanol content and the additives used. As the ethanol content increases in diesel fuel, smoke, CO_2 emissions and NO_X emissions decrease [15]. At idle and low load conditions, the blended fuel lowers smoke emissions [16]. However, unregulated compounds are expected to increase with blending.

Detailed investigations are needed to document the exact extent of the increase in unregulated emissions due to ethanol blending in diesel fuels.

5. TEST ENGINE, TEST CYCLE AND BLEND PREPARATION

In the present study, a multi-cylinder diesel engine was considered for testing unregulated emissions from ethanol diesel blends. Table 4 shows brief engine specifications that were used during this investigation. A multi-cylinder inline direct injection diesel engine was used for diesel and diesel-ethanol fuel blend testing.

The testing was conducted following the ISO 8178 C1 standard test procedure, which consists of an 8-mode cycle designed to simulate various engine operating conditions encountered in real-world applications, as depicted in Figure 3.

Table 4. Engine specifications

Engine Characteristics	
Engine Make	TMT
Engine Model	ED PT3
Engine Type	INLINE DI NA
Engine Speed (Rated RPM)	2150
Engine Capacity (L)	3.0

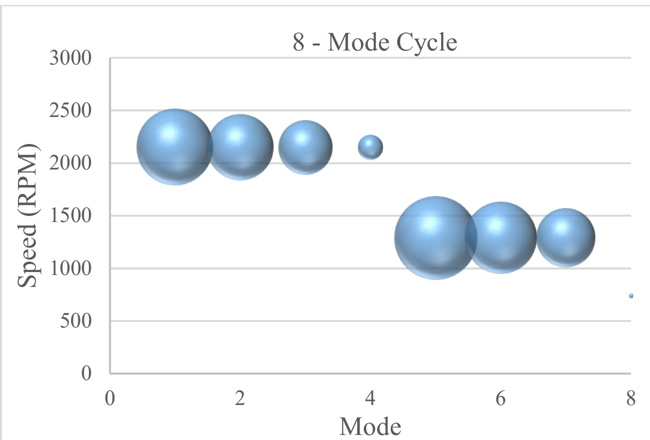

Figure 3. ISO 8178 test cycle

ISO 8178-C1, also known as the "Non-Road Steady Cycle", is a test cycle used to determine the emission levels of non-road engines. This test procedure encompasses a range of engine loads and speeds, providing a comprehensive assessment of emission characteristics under diverse operating scenarios. Various operating modes as per the ISO 8178 C1 (8-mode) test procedure are shown in Figure 3. The engine boundary conditions like lubricating oil temperature, coolant temperature, and intake air temperature and pressure were maintained for diesel (D0) and diesel-ethanol blend (D20) for the repeatability of the results. A base diesel engine and 20% ethanol blended fuel (D20) were considered for measurement and analysis of engine exhaust to study the emission pattern of formaldehyde, aldehydes, ketones, etc.

The D20 fuel blend, which consists of 20% ethanol and 80% diesel by volume, was prepared using diesel, ethanol, and a blending additive. Figure 4 illustrates the components used in the preparation of the D20 blend. Blending diesel and ethanol poses a challenge due to the significant differences in their physical and chemical properties, such as polarity, density, and solubility. Diesel is a non-polar hydrocarbon, whereas ethanol is a polar substance with a high affinity for water, resulting in immiscibility when the two are mixed directly. This disparity often leads to phase separation, especially under varying temperature and humidity conditions, thereby affecting the stability and homogeneity of the blend.

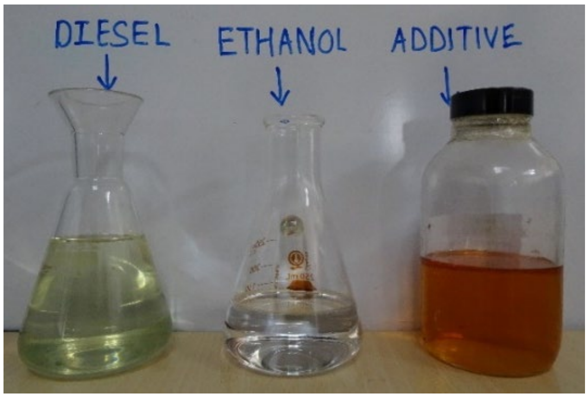

Figure 4. Diesel, ethanol and additive used for blend preparation

To overcome these challenges and ensure a stable and uniform fuel mixture, a suitable additive was incorporated into the D20 blend formulation. The additive acts as a co-solvent and emulsifier, facilitating the blending of ethanol with diesel by reducing the interfacial tension between the two fluids and promoting miscibility. Moreover, the additive not only stabilizes the blend but also enhances certain properties of the fuel, such as improving lubricity, increasing cetane number, or providing anti-corrosive effects, which contribute to better engine performance and reduced wear.

(a) D20 without additive

(b) D20 with additive

Figure 5. D20 fuel with and without additive

Figure 5 demonstrates the visual differences between D20 fuel with and without the additive. Without the additive, the blend shows signs of phase separation, indicating that the ethanol and diesel do not mix effectively. In contrast, the D20 fuel containing the additive appears homogeneous and stable, underscoring the importance of the additive for achieving a proper blend formulation. This highlights the necessity of using an additive in diesel-ethanol blends to maintain fuel stability and enhance blend characteristics, thereby making the D20 blend suitable for practical use in internal combustion engines.

6. EXPERIMENTATION AND DATA COLLECTION

In this study, emission samples were collected in the dinitrophenylhydrazine (DNPH) cartridges intergraded with the emission system of the engine test cell and the samples were analysed using high performance liquid chromatography. The carbonyl group reaction of DNPH species is shown in Figure 6. The process followed for sample collection is depicted in the form of a flow chart in Figure 7.

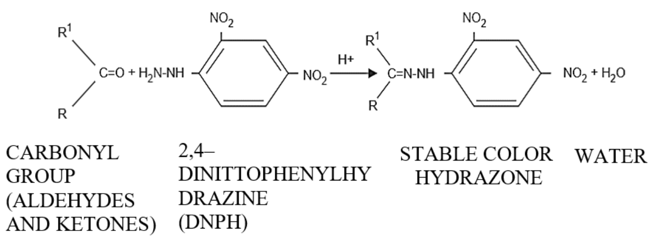

Figure 6. Carbonyl group reaction with DNPH [17]

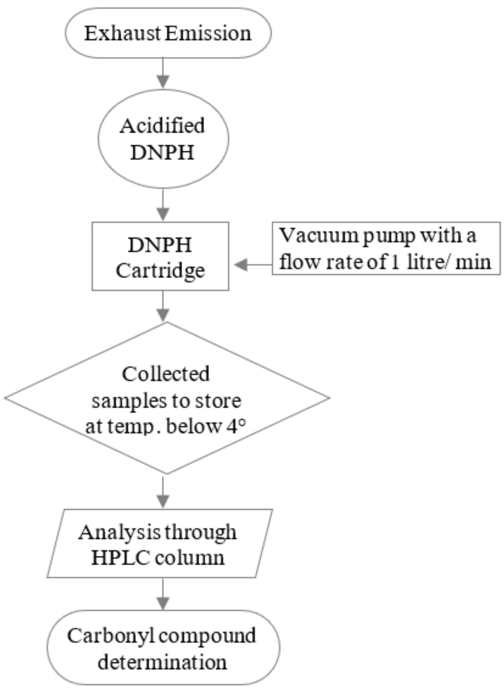

Figure 7. Sample collection process flow chart

During the sample collection process, a consistent flow rate of 1 litre per minute (LPM) was meticulously maintained using a calibrated rotameter to ensure the accuracy and reliability of the data. The sampling was conducted over a total duration of 16 minutes, corresponding to an 8-mode test cycle, with each mode lasting for 2 minutes. This approach allowed for a comprehensive assessment of the emissions across various engine operating conditions. The samples were collected using a 2, 4-dinitrophenylhydrazine (DNPH) cartridge, which is well-suited for capturing carbonyl compounds from exhaust gases.

Quality assurance procedure:

To ensure the accuracy of the flow rate and to confirm the integrity of the sample collection system, measurements were taken at both the inlet and outlet of the sampling setup using an air flow calibrator with a range of 1 to 20 LPM. This dual-point measurement procedure was implemented to verify leak-free operation throughout the entire sampling process, thereby ensuring that the sample collection was conducted under optimal conditions. To ensure the repeatability of the process, two samples were measured (D20-S1 and D20-S2) and analyed. By maintaining a precise and stable flow rate, the study aimed to minimize measurement errors and enhance the reliability of the collected data for subsequent analysis of unregulated pollutants.

Engine dynamometers, exhaust gas analysers, exhaust gas dilution systems for particle collection, and suitable data-acquisition systems available in the laboratories to regulate and monitor the engine test runs were used for this research study.

The specifications of the engine used in this research are mentioned in Table 4. The testing was performed on a variable speed engine based on ISO 8178 C1 (8-mode) test cycle. In the initial part of the study, pure diesel (D0) was used, thereafter the diesel - ethanol blended fuel (D20) was used for the testing. Using cartridges of dinitrophenylhydrazine (DNPH), carbonyl compounds were extracted from the exhaust gases. The unregulated emission sample was collected from the same location as that of the regulated particulate samples. An acetonitrile/water solution was used to extract the DNPH derivatives. Emissions of 13 aldehydes and 2 ketones were examined using high-performance liquid chromatography (HPLC) technology. Formaldehyde and acetaldehyde emissions were specially focused due to their adverse effects. Other aldehydes analysed included acrolein, propionaldehyde, crotonaldehyde, methacrolein, butyraldehyde, benzaldehyde, valeraldehyde, m-tolualdehyde and hexanal.

Figure 8 shows the schematic layout of the experimental set-up used during the sample collection and engine testing. AVL make steady state dynamometer, Horiba make emission analyser for measurement of gas emissions like HC, CO, NOx, and CO_2 and AVL make particulate measuring system were used during the testing. The HPCL column specifications are elaborated in Table 5.

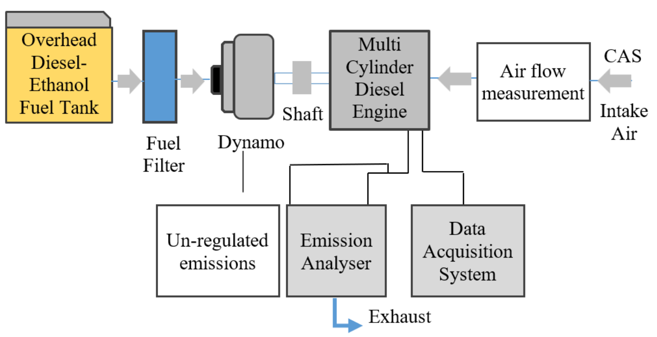

Figure 8. Engine testing schematic diagram

Table 5. HPLC column specifications

Particulars	Specifications
Column details	Shim-Pack, C18, 250 mm, 5 µm
Column temp	40°C
Mobile phase	Water: THF (8:2), Acetonitrile
Sample	Sample in DNPH
Injection	10 µl
Flow rate	1.5 ml
Detector	UV, 365 nm
Run time	40 mins

7. TEST PROCEDURE

Engine testing was carried out as mentioned in the previous section. 2-4 dinitrophenyl hydrazine was used as a base reagent for carbonyl compounds. The DNPH cartridge was used in the present study because it is more accurate than the conventional impinger system. The DNPH cartridge was connected with the emission measurement system to collect the carbonyl compounds as follows:

(1) The samples in the cartridge system were collected in the absorbent cartridges which contained DNPH solution.

(2) The samples formed derivatives of DNPH after passing through the cartridges.

(3) The cartridges with samples were stored at the required temperature and later, they were analysed with the help of HPLC (high performance liquid chromatography).

(4) With the help of a chromatogram of HPLC, the emissions of different carbonyl compounds were obtained.

The schematic diagram of the HPLC system, which consisted of a pump, injector, column, detector, and an integrator or acquisition and display system is shown in Figure 9.

A more detailed schematic of HPCL column is shown in Figure 10.

The complete sampling procedure for carbonyl compounds comprising of raw sample collection, sampling, stabilisation and analysis is shown in Figure 11. The actual test set up photographs are shown in Figure 12.

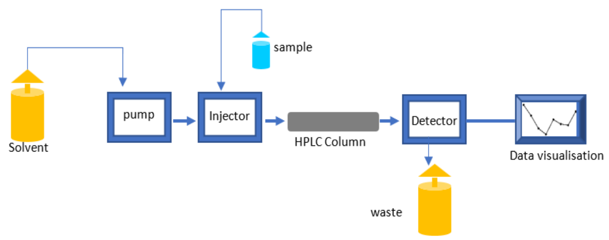

Figure 9. Schematic diagram of the HPLC system for obtaining emission chromatograms

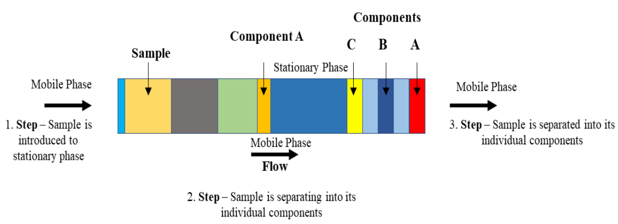

Figure 10. HPLC column system

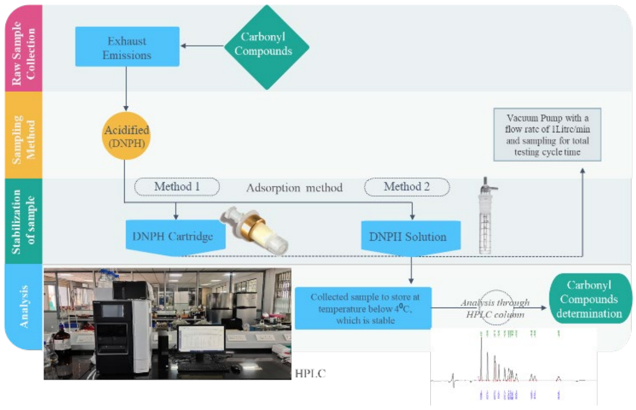

Figure 11. Sampling procedure for carbonyl compounds

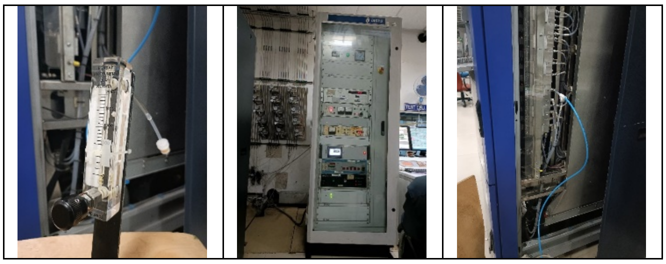

Figure 12. Sample collection test set-up for unregulated emissions

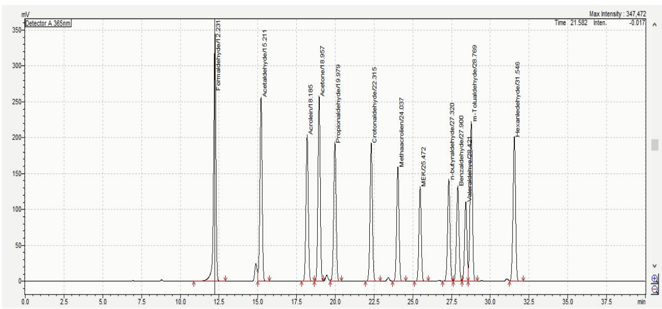

Figure 13. Typical elution profile obtained from the HPLC system

A typical elution profile resulting from the HPLC column is shown in Figure 13. In this profile, each peak corresponds to a particular un-regulated emission. The amplitude and the time frame of each peak depicts the magnitude and type of the un-regulated emission. The entire un-regulated emissions data obtained from HPLC for ethanol diesel blend and pure diesel is presented and discussed in the next section.

8. RESULTS AND DISCUSSION

The engine under study was initially tested neat diesel (D0) and later tested with diesel-ethanol blended fuel (D20). The testing with D20 was carried out with two identical samples designated as D20-S1 and D20-S2. Table 6 elaborates the emission values of each pollutant for D0, D20-S1 and D20-S2. In total, 15 carbonyl compounds were analyzed of which 9 components were found to be below detection limit (BDL).

The results clearly indicate that blending diesel with ethanol has a substantial impact on the levels of specific carbonyl compounds emitted in the exhaust gases. Notably, the concentrations of formaldehyde and acetaldehyde were found to increase significantly when diesel-ethanol blended fuel was used, in comparison to pure diesel fuel. The formaldehyde concentration rose by approximately 115%, suggesting that the presence of ethanol promotes the formation of this compound during combustion. Even more prominent was the increase in acetaldehyde levels, which surged by nearly 3300%, indicating a significant rise in its formation due to the introduction of ethanol into the fuel mixture. This noticeable increase can be attributed to the higher oxygen content in ethanol, which enhances the oxidation of hydrocarbons, thereby facilitating the formation of oxygenated species such as aldehydes.

Table 6. Un-regulated emission results

Sr. No.	Components	D0	D20-S1 (µg)	D20-S2 (µg)
1	Formaldehyde	7.25	12.99	18.26
2	Acetaldehyde	1.89	70.37	57.91
3	Acrolein	0.35	0.58	0.78
4	Acetone	3.45	0.36	0.41
5	Propionaldehyde	BDL	0.14	0.12
6	Crotonaldehyde	0.65	0.32	0.47
7	Butyraldehyde	BDL	BDL	BDL
8	Benzaldehyde	2.16	1.9	2.02
9	Isovaleraldehyde	BDL	BDL	BDL
10	Valeraldehye	BDL	BDL	BDL
11	o-Tolualdehyde	BDL	BDL	BDL
12	m-Tolualdehyde	BDL	BDL	BDL
13	p-Tolualdehyde	BDL	BDL	BDL
14	Hexanledehyde	BDL	BDL	BDL
15	2,5-demethyl benzaldehyde	BDL	BDL	0.48
	Total Carbonyl	15.755	86.666	80.450

Conversely, the concentration of acetone in the exhaust emissions showed a clear reduction with the use of diesel-ethanol blends. Specifically, acetone levels decreased by about 88% compared to emissions from pure diesel. This significant reduction could be due to the change in the combustion characteristics in the presence of ethanol, which favors the formation of other oxygenated compounds over acetone. The changes in the levels of these carbonyl compounds highlight the complex nature of combustion chemistry when alternative fuels are used and underscore the need to understand how such blends affect the formation of various unregulated pollutants.

From these results, it is evident that the levels of formaldehyde and acetaldehyde increase significantly when diesel is blended with ethanol, as compared to diesel alone. Additionally, the levels of acetone decrease significantly with diesel-ethanol blending. Formaldehyde levels increased by approximately 115%, while acetaldehyde levels increased by almost 3300% with diesel-ethanol blended fuel when compared to pure diesel. In contrast, acetone levels decreased by 88% with diesel-ethanol blended fuel when compared to diesel.

It is important to note that these pollutants are measured in µg, which is why a substantial difference is observed. The levels of various unregulated emissions are illustrated in Figure 14 for better understanding. When all the constituents are combined, there is a 430% increase in unregulated emissions levels observed with diesel-ethanol blended fuel as compared to pure diesel.

These findings provide crucial information about how diesel-ethanol blends affect emissions. They further contribute to a more complete understanding of the impact of alternative fuels on engine exhaust composition in the context of literature published in this field.

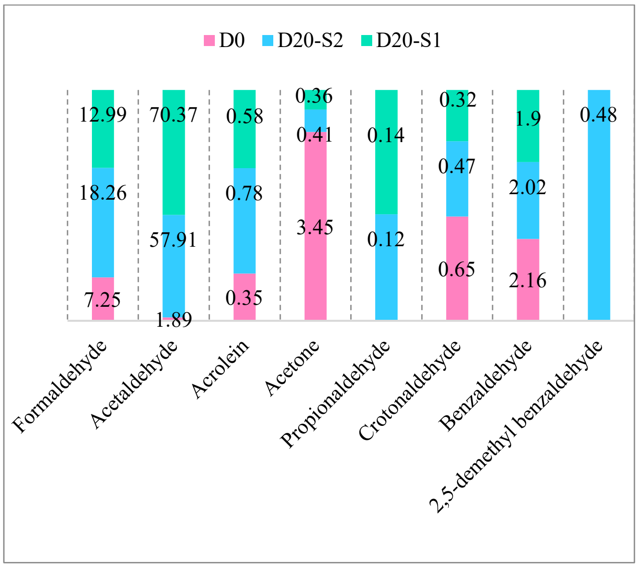

Figure 14. Comparison of emissions of un-regulated pollutants with different blends

The formulation of formaldehyde, acetaldehyde, and acetone is further explained in the following section for a more detailed understanding to help decide appropriate mitigation strategies.

A. Formaldehyde Formation

When diesel and ethanol are burned together, the process results in the production of formaldehyde (CH_2O) through complex chemical reactions involving both fuels. This process is described as follows:

Initial Combustion:

Diesel and ethanol are vaporized and mixed with air before ignition. During the compression stroke, the temperature and pressure rise, which initiates combustion.

Primary Combustion:

During the early phases of combustion, the hydrocarbons present in diesel fuel undergo pyrolysis and oxidation reactions, leading to the breakdown of larger hydrocarbon fragments into smaller ones. These smaller fragments react with oxygen to form carbon dioxide (CO_2) and water vapor (H_2O). Similarly, ethanol also undergoes similar combustion reactions.

Intermediate Species Formation:

In the combustion chamber, intermediate products from both diesel and ethanol combustion can react to form formaldehyde under high temperatures and pressures. These intermediate products include free radicals such as methyl (CH3) and hydroxyl (OH) radicals, which combine to create methanol (CH3OH) and hydroxymethyl (CH_2OH) radicals. These radicals then react with oxygen to produce formaldehyde.

Formaldehyde Formation:

The hydroxymethyl radicals (CH_2OH) formed from the intermediate species can undergo further reactions, such as hydrogen abstraction and oxygen addition, leading to the formation of formaldehyde (CH_2O). The reactions involved in the Formaldehydes formation are described as follows.

Oxidation of Hydrocarbons:

In the combustion of diesel and ethanol, hydrocarbons present in both fuels undergo oxidation reactions with oxygen (O_2) from the air. These reactions produce carbon dioxide (CO_2) and water vapor (H_2O) as primary combustion products.

Diesel:

$$C_nH_m + \left(\frac{n}{2} + \frac{m}{4}\right) O_2 \rightarrow nCO_2 + \frac{m}{2} H_2O$$

Ethanol:

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

Formation of Methanol:

In the presence of oxygen, methyl radicals ($CH_3.$) are formed from hydrocarbon fragments. These radicals combine with another radical or react further to form methanol (CH_3OH):

$$CH_3. + OH \rightarrow CH_3OH$$

Formation of Formaldehyde:

Thereafter, methanol undergoes further oxidation reactions to produce formaldehyde. This can occur through multiple steps, including hydrogen abstraction and oxygen addition reactions.

$$CH_3OH + OH \rightarrow CH_2OH + H_2O$$
$$CH_2OH + O_2 \rightarrow CH_2O + H_2O$$

It is important to note that formaldehyde formation is influenced by various factors including temperature, pressure, fuel composition, combustion efficiency, and engine design. In diesel-ethanol blends, ethanol's unique combustion properties, such as its higher oxygen content and different chemical structure compared to diesel, affects the combustion process for the formation of formaldehyde and other byproducts.

B. Acetaldehyde Formation

In the combustion process of diesel-ethanol blends, acetaldehyde (CH_3CHO) forms through several pathways, including the oxidation of ethanol and the subsequent reactions of its oxidation intermediates. A simplified overview of how acetaldehyde is formed during the combustion of diesel and ethanol together is as follows:

Ethanol Vaporization and Mixing:

In a diesel-ethanol engine, ethanol is blended with diesel fuel. During the intake stroke, the blended fuel mixture is vaporized and mixed with air in the combustion chamber.

Ignition and Combustion:

During the compression stroke, the air-fuel mixture is compressed, leading to an increase in temperature and pressure. Eventually, the mixture reaches its autoignition temperature, leading to combustion. Both diesel and ethanol undergo combustion reactions, producing heat, pressure, and various combustion intermediates.

Ethanol Combustion:

Ethanol undergoes oxidation reactions, breaking down into smaller molecules and producing various intermediates. One of the primary oxidation products of ethanol is acetaldehyde. The combustion of ethanol can be represented by the following simplified equation:

$$C_2H_5OH + 3O_2 \rightarrow 2CH_3CHO + 3H_2O$$

This equation illustrates the conversion of ethanol (C_2H_5OH) into acetaldehyde (CH_3CHO) and water vapor (H_2O) in the presence of oxygen (O_2).

C. Acetone Formation

Acetone (CH_3COCH_3) forms in the combustion of diesel-ethanol blends through various pathways, primarily involving the oxidation of ethanol and subsequent chemical reactions. Vaporization and Mixing, Ignition and Combustion & Ethanol Combustion processes remain the same.

Acetone Formation:

Acetone forms from acetaldehyde and other combustion intermediates through various pathways, including:

Condensation:

Acetaldehyde (formed from ethanol combustion) reacts further through condensation reactions with other reactive intermediates, such as methyl radicals (CH_3), to form acetone.

Oxidation:

Acetaldehyde and other intermediates undergo further oxidation reactions, leading to the formation of acetone. For example, acetaldehyde reacts with hydroxyl radicals (OH) or molecular oxygen (O_2) to produce acetone.

$$C_2H_5OH + 3O_2 \rightarrow 2CH_3CHO + 3H_2O$$
$$2CH_3CHO \rightarrow CH_3COCH_3 + CH_3CHOHCHO$$

This reaction involves the condensation of two molecules of acetaldehyde to form acetone (CH_3COCH_3) and an intermediate compound, acetal ($CH_3CHOHCHO$).

D. Mitigation Strategies for Un-Regulated Emissions

Reducing the emissions of formaldehyde, acetaldehyde, and acetone from diesel-ethanol engines is a complex process that requires a comprehensive approach. This approach involves addressing combustion efficiency, fuel composition, and emission control technologies. Some of the mitigation strategies that can be used to reduce these pollutants are presented below:

Optimize Engine Design and Operation:

(1) Improve combustion efficiency by optimizing engine parameters such as injection timing, compression ratio, and air-fuel ratio.
(2) Use advanced combustion technologies like homogeneous charge compression ignition (HCCI), stratified charge combustion, or low-temperature combustion (LTC) to minimize incomplete combustion.
(3) Implement exhaust gas recirculation (EGR) to reduce combustion temperatures and decrease the formation of aldehydes.

Fuel Formulation:

(1) Optimize the blend ratio of diesel and ethanol to achieve

better combustion characteristics and reduce emissions of aldehydes.
(2) Use higher-quality ethanol with lower impurities to minimize the formation of aldehydes and ketones.
(3) Incorporate additives into the fuel formulation that promote more complete combustion and reduce the formation of aldehydes and ketones.

Exhaust Gas Aftertreatment:
(1) Install diesel oxidation catalysts (DOCs) or selective catalytic reduction (SCR) systems to convert aldehydes and ketones into less harmful compounds.
(2) Utilize particulate filters to trap particulate matter and organic compounds, including aldehydes and ketones, from the exhaust stream.

Advanced Engine Control and Calibration:
(1) Implement advanced engine control strategies and calibration techniques to optimize fuel injection parameters and exhaust gas recirculation rates for minimizing aldehyde and ketone formation.
(2) Utilize dynamic control algorithms to adjust engine operation in real-time based on operating conditions and emission requirements.

The emissions of formaldehyde, acetaldehyde, and acetone from diesel-ethanol engines can be reduced effectively by implementing the above-mentioned mitigation strategies.

These strategies will help improve air quality, environmental sustainability and human health due to inhaled air. Future research and development efforts in engine technology and fuel formulation will continue to drive advancements in un-regulated emission reduction strategies for diesel-ethanol engines

E. Limitations of the Method Used for the Collection of Samples and Analysis of Un-Regulated Emissions

i. Reactivity with Other Compounds:

Nitrogen dioxide (NO_2) and carbon monoxide (CO) in the sampled air can react with DNPH solution, consuming the DNPH and possibly underreporting carbonyl contents, especially formaldehyde and acetaldehyde. However, to overcome this, in our study, the collected sample was stored below 4℃ to avoid any secondary reaction with other pollutants present in the exhaust gas. Additionally, a DNPH cartridge was used in place of a DNPH solution, which reduces the problem of underreporting of carbonyl contents and evaporation.

ii. Sampling Conditions:

The effectiveness of the DNPH method can be influenced by environmental conditions such as temperature and humidity. High humidity levels can lead to hydrolysis of the derivatives, affecting the accuracy of the measurements. As explained earlier, in our study, the collected sample was stored below 4℃ till the completion of the analysis using HPLC.

iii. Storage Stability:

Samples collected using DNPH cartridges have stability issues over time. If not analyzed promptly, the derivatives can degrade, leading to inaccurate quantification of the original compounds. In our study, the analysis was completed within 24 hours of the test to overcome above mentioned issues.

iv. Sampling Time Variation

Since the measurement of unregulated emissions lacks a defined protocol. The concentration and final outcomes may be impacted by changes in the sample period and flow rate. Therefore, a standard technique needs to be developed in order to acquire repeated outcomes.

F. Environmental and Health Implications

The environmental and health implications of each un-regulated pollutant are shown in Table 7. With the use of diesel-ethanol (D20) blended fuel some of the carbonyl pollutants increased while others decreased as compared to base diesel.

Table 7. Environmental and health implications

Emissions	Health and Environmental Effects	Effects with D20 in the Present Study
Formaldehyde	Respiratory irritation, headaches, and potential carcinogenic effects, while also contributing to environmental pollution through its role in the formation of ground-level ozone and degradation of air quality.	Increased
Acetaldehyde		
Acrolein	Highly toxic aldehyde causes severe respiratory irritation and distress upon exposure and also affects the environment.	Increased
Acetone	Eye and respiratory irritation, headaches, and dizziness, while also posing risks to liver and kidney function. It harms aquatic life.	Decreased
Propionaldehyde		Increased
Crotonaldehyde	Respiratory irritation, skin burns, and potential carcinogenic effects. Volatile organic compound (VOC) that can degrade air quality and harm aquatic ecosystems through runoff.	Decreased
Benzaldehyde	Skin irritation, respiratory issues, and headaches. Toxicity to aquatic life and rapid biodegradation.	Decreased

G. Comparison of Results with Existing Literature:

In this sub-section, the results discussed in earlier sections are compared with other similar contemporary studies available in the literature. Primarily, the current study reports that formaldehyde and acetaldehyde emissions increased by 115% and 3293%, respectively, whereas acetone emissions were reduced by 89% for D20 fuel over base diesel (D0) in a three-cylinder diesel engine used for non-road application, tested over 8 mode mass emission test cycle as per ISO 8178-C1 standard. The engine was operating in the range of 1300-2150 rpm.

In the first comparison, Song et al. [18] investigated carbonyl compound emissions in a six-cylinder heavy-duty diesel engine fueled with diesel and diesel-ethanol blend (15% by volume ethanol). The engine was tested over 13 mode test cycles as per ECE R-49 test standard. The authors reported an increase in formaldehyde, acetaldehyde, and acetone emissions by 451%, 143%, and 241%, respectively, at the 1200 – 2600 rpm range. Although the engine type, test cycle, and ethanol blending percentage in the present study are different from those employed by Song et al., a significant increase in formaldehyde and acetaldehyde emissions is evident in both studies. The acetone emissions have been reported to increase by Song et al., whereas they have decreased due to ethanol blending in the present study.

In the second comparison, Li et al. [19] investigated regulated and unregulated emissions in a four-cylinder direct injection diesel engine fueled with diesel and diesel-ethanol blend (15% by volume ethanol). The engine was tested for different IMEP ranging from 3-9 bar. The authors reported an increase in formaldehyde and acetaldehyde emissions by 200% and 300%, respectively, at 1500 rpm. Although the engine type, test procedure, and ethanol blending percentage in the present study are different from those employed by the study [19], a significant increase in formaldehyde and acetaldehyde emissions is evident in both studies. The acetone emissions have not been reported by the study [19] for comparison with the present study.

In the third comparison, Yan et al. [20] investigated both regulated and unregulated emissions in a single-cylinder diesel engine without any modifications. The engine was fueled with a diesel and a diesel-ethanol blend of 20% (E20). The engine was tested at constant speed and constant torque outputs. At a rated RPM of 1500, the formaldehyde and acetaldehyde emissions of E20 increased by 4.2% and 200%, respectively, at the rated load compared to diesel. However, acetone emissions were not measured in this study. Although the engine type, test cycle, and ethanol blending percentage in the present study are different from those employed by Yan et al., an increase in formaldehyde and acetaldehyde emissions is evident in both studies.

In the fourth comparison, He et al. [11] investigated the unregulated emissions of ethanol-diesel blend percentage of up to 30% (E30) by volume. The blends were tested on a twin cylinder naturally aspirated direct injection diesel engine at constant speed for various load conditions. The authors reported that at rated RPM and rated power output, the formaldehyde emissions of E30 increased by about 2-3% compared to that of diesel but showed a negligible increase when compared to E10. However, the Acetaldehyde emissions increased by almost 150% and 66% for E30 and E10, respectively, as compared to that of diesel emissions. This study also concluded that there is a rise in aldehyde and formaldehyde emissions when ethanol is added to diesel, supporting the findings of the present study.

In the fifth comparison, Haupt et al. [21] investigated the effects of Ethanol fuel on a 9L HD Euro III diesel engine equipped with an aftercooler and a turbocharger. The engine was tested in the European Stationery Cycle (ESC) stationery cycle. The authors reported that the system produced about 1600% and 9800% more formaldehyde and acetaldehyde emissions, respectively, as compared to the baseline diesel engine. This study concluded that there is a rise in aldehyde and formaldehyde emissions when ethanol is used as a fuel, indirectly supporting the findings of the present study.

H. ANOVA of Un-Regulated Emissions in Terms of Fuel Properties

In the present study, a two-way ANOVA test was conducted to examine the statistical significance of the measured un-regulated emissions (formaldehyde, acetaldehyde, acetone, and, acrolein) in terms of critical fuel properties of blended diesel (Gross Calorific Value, Cetane Number, and Flash Point) that witnessed a significant deviation from the corresponding base diesel fuel properties.

(1) Effect on Formaldehyde

Table 8 shows the ANOVA results for formaldehyde emissions. From the analysis, it can be seen that the value of P for cetane number and Gross CV is less than 0.05. Hence, these properties have statistically significant effects on formaldehyde emissions. The higher the F value, the more is the significance. The F value of Gross CV is higher than the Cetane Number, which means that Gross CV is the most significant factor for the formation of formaldehyde due to ethanol blended diesel fuel.

Table 8. ANOVA output for formaldehyde

	Flash Point	**Cetane Number**	**Gross CV**
S of Sq.	232.9439	1611.019	113572981.1
Dof	1	1	1
M of Sq.	232.9439	1611.019	113572981.1
F	**0.841727**	**55.04787**	**1078.384**
P-value	**0.455755**	**0.017686**	**0.000926**
F crit	18.51282	18.51282	18.51282

(2) Effect on Acetaldehyde

Table 9 shows the ANOVA results for acetaldehyde emissions. From the analysis, it can be seen that the value of P for Gross CV is less than 0.05, which means that Gross CV is the only statistically significant factor for the formation of acetaldehyde due to ethanol blended diesel fuel.

Table 9. ANOVA output for acetaldehyde

	Flash Point	**Cetane Number**	**Gross CV**
S of Sq.	39.879225	344.4736	113113541.2
Dof	1	1	1
M of Sq.	39.879225	344.4736	113113541.2
F	**0.032475584**	**0.35132577**	**1064.407537**
P-value	**0.873594546**	**0.613456298**	**0.000938168**
F crit	18.51282	18.51282	18.51282

(3) Effect on Acetone

Table 10 shows the ANOVA results for acetone emissions.

From the analysis, it can be seen that the value of P for all three properties (Gross CV, Cetane Number, and Flash Point) is less than 0.05, which means all three properties are statistically significant factors for the formation of acetone. However, based on higher F value, Gross CV is the most significant impact on the formation of acetone due to ethanol blended diesel fuel.

Table 10. ANOVA output for acetone

	Flash Point	**Cetane Number**	**Gross CV**
S of Sq.	614.1723063	2465.867306	113775982.2
Dof	1	1	1
M of Sq.	614.1723	2465.867	1.14E+08
F	**23.48125**	**175.1428**	**1080.467**
P-value	**0.026513152**	**0.005661187**	**0.000924243**
F crit	18.51282	18.51282	18.51282

(4) Effect on Acrolein

Table 11 shows the ANOVA results for acrolein emissions. From the analysis, it can be seen that the value of P for all three properties (Gross CV, Cetane Number, and Flash Point) is less than 0.05, which means all three properties are statistically significant factors for the formation of acrolein. However, based on higher F value, Gross CV is the most significant impact on the formation of acrolein due to ethanol blended diesel fuel.

Table 11. ANOVA output for Acrolein

	Flash Point	Cetane Number	Gross CV
S of Sq.	685.654225	2607.1236	113805904
Dof	1	1	1
M of Sq.	685.6542	2607.124	1.14E+08
F	**26.44891**	**221.7347**	**1080.775**
P-value	**0.024540117**	**0.004479612**	**0.00092398**
F crit	18.51282	18.51282	18.51282

9. CONCLUSIONS

Blending ethanol with diesel fuel leads to different combustion characteristics, as ethanol has a higher oxygen content and a different chemical structure compared to diesel alone. This blending changes the combustion process and kinetics, which results in incomplete combustion. Factors such as inadequate combustion chamber temperature and pressure conditions, improper air-fuel mixing, or heterogeneous combustion contribute to incomplete combustion. Also, the Diesel-Ethanol blend has a lower cetane number compared to diesel, leading to delayed ignition and increased formation of carbonyl compounds during the combustion process. species due to enhanced thermal decomposition of the fuel.

In this study, pure diesel and 20% ethanol blended diesel fuels were used in a multi-cylinder diesel engine to measure and compare unregulated emissions emanating from them under an ISO 8178 C1 (8-mode) test cycle. The emissions of 13 aldehydes and 2 ketones were captured using a 2-4 dinitrophenyl hydrazine (DNPH) cartridge and analysed using a high-performance liquid chromatography (HPLC) system. The key findings of the present study are summarised as follows:

(1) When diesel is blended with ethanol (D20), the level of formaldehyde increases by approximately 115% in comparison to pure diesel.
(2) Additionally, the level of acetaldehyde increases by 3300% with D20 as compared to pure diesel.
(3) On the other hand, the level of acetone decreases by 88% with D20 in comparison to diesel.
(4) When all the constituents are considered, there is a 430% increase in unregulated emissions levels observed with D20 as compared to pure diesel.
(5) It is important to note that the operating conditions of the engine, such as load, speed, and temperature influence the combustion process and the formation of aldehydes. Under certain operating conditions (such as low load or low temperature) incomplete combustion is more likely to occur, leading to higher emissions of formaldehyde and acetaldehyde.
(6) ANOVA results showed that the Gross Calorific Value of the fuel has the most significant impact (among Cetane Number, Flash Point, and Gross Calorific Value) on the formation of formaldehyde, acetaldehyde, acetone, and acrolein.

Ethanol, with oxygen in its molecular structure, increases oxygen availability during combustion. This promotes the formation of oxygenated intermediates, such as formaldehyde and acetaldehyde, through reactions with fuel radicals and molecular oxygen. In order to address the issue of incomplete combustion and the formation of carbonyl emissions, it is essential to optimize engine design and combustion parameters in the future. Additionally, it is possible to develop various additives for diesel-ethanol blending, which could improve the blended fuel properties and enhance engine combustion. This improved engine combustion could result in a reduction of unregulated emissions. To identify the optimal blend that can match the performance and emission of base diesel, it is important to test various fuel blends such as D5, D10, and D15 in the future.

The potential mitigation strategies recommended for future research in this study include engine design and operation optimization (such as HCCI, LTC, and EGR), optimum fuel formulation (such as use of higher-quality ethanol with lower impurities), selection of suitable exhaust gas after-treatment system (such as DOC, SCR), and advanced engine control and calibration strategies which can be employed to bring down aldehyde emissions from diesel-ethanol blended engines.

Future studies may be conducted to further evolve such mitigation strategies, contributing towards a healthier environment for our planet.

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