

POTENTIALS FOR OZONE FORMING FROM OFF-ROAD HEAVY-DUTY DIESEL ENGINE'S EMISSIONS

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Abstract: Ground level ozone is one major secondary pollutant which is formed in the atmosphere by a variety of photochemical reactions involving volatile organic compounds and oxides of nitrogen in the presence of sunlight. Due to their reactivity, the exhaust emissions from heavy duty diesel engines are of particular concern and it is desirable to reduce the ozone forming potential of the exhaust emissions by reducing the mass of exhaust emissions. This study investigates the effect of retrofitted after-treatment devices and ultra-low sulfur diesel fuels on the ozone forming potential of exhaust emissions from heavy-duty off-road diesel engines. Specifically, the objective was to determine the effect of two diesel particulate filters and two ultra-low sulfur diesel fuels on the ozone forming potential from the 3 test diesel engines retrofitted with and without passive diesel particulate filters.

Keywords: HEAVY-DUTY DIESEL ENGINE EMISSIONS, OZONE FORMING POTENTIAL, AFTERTREATMENT DEVICE

1. Introduction

Once released into the atmosphere, the pollutants from Heavy-Duty Diesel Engines (HDDE) are subject to dispersion and transport and at the same time to chemical and physical transformations into secondary pollutants. The secondary pollutants can be at times more harmful than precursors. Ground level ozone (O₃) is one major secondary pollutant which is formed in the atmosphere by a variety of photochemical reactions involving volatile organic compounds (VOC) and oxides of nitrogen (NO_x) in the presence of sunlight. Due to their reactivity, the exhaust emissions from HDDE are of particular concern and it is desirable to reduce the ozone forming potential of the exhaust emissions by reducing the mass of exhaust emissions. Retrofitting an engine with after-treatment device and powering it with ultra-low sulfur diesel (ULSD) fuel is an effective way to reduce the emissions and hence the ozone forming potential of the emissions.

HDDE exhaust contains Total Particulate Matter (TPM) composed of elemental carbon, ash, organic fraction and sulfate particulates; NO_x, hydrocarbons and its derivatives and polycyclic aromatic hydrocarbons (PAHs). Once released into the atmosphere, these pollutants are detrimental to human health and the flora and fauna. Various regulatory bodies around the world are creating legislation to control exhaust emissions from HDDE installed on on-road and off-road equipment. One of the many ways to control exhaust emissions is by the use of exhaust after-treatment devices. The different types of after-treatment devices used in HDDE include Diesel Oxidation Catalysts (DOCs), NO_x Adsorber Catalysts, Urea-Selective Catalytic Reduction (SCR) catalysts, Diesel Particulate Filters (DPFs), Lean NO_x Catalysts and Plasma-Assisted Catalysts [1]. The choice of using the appropriate after-treatment device depends on the particular application. The two most popular and commonly used systems among these are the DPF and DOC. DPF is generally used when a high reduction in PM is desired, whereas the DOC is preferred when it is more important to reduce the soluble organic fractions (SOF) and hydrocarbons (HC).

The first objective of this study was specifically to determine the effect of two diesel particulate filters - Engelhard DPXTM and Johnson Matthey CRTTM, and two ULSD fuels on the ozone forming potential (OFP) of exhaust emissions from HDDE. DPXTM is engineered to be a fully passive DPF. CRTTM is also a fully passive DPF but the oxidation process is different. It has been shown that NO₂ is more effective in oxidizing carbon than oxygen and oxidation can occur at low (about 300 °C to 350 °C) temperatures without the aid of any catalyst [2]. For this reason CRTTM first generates NO₂ by catalytic oxidation of NO according to the following reaction:



and then uses the generated NO₂ to oxidize the carbon.



There are many factors that influence the OFP of emissions from HDDE: 1) engine design, 2) fuel, 3) after-treatment device used, 4) control system of engine, 5) engine cycle. To control the quality of atmospheric air it is important to investigate how these factors affect the OFP of emissions from HDDE.

All species in the exhaust emissions do not have the same reactivity; some of them contribute heavily while others have almost negligible ozone impact. A study done to investigate the effect of alkenes on reactivity of emissions indicates that alkenes are among the most photo-chemically reactive components in emissions from vehicles [3]. Aromatic compounds also have large impact on ozone formation. Interestingly, most of the aromatic compounds are inherently present in diesel exhaust emissions irrespective of the aromatic content of the fuel or operating condition [4]. Apart from alkenes and aromatics, aldehydes also contribute significantly towards the ozone forming potential of diesel exhaust [5].

The second objective of this study was to determine distance specific reactivity of emissions from HDDE. This can be achieved by multiplying the reactivity of each VOC by the emission rate of that particular VOC. But, it is of utmost importance to select appropriate reactivity scale before proceeding with any calculations.

2. Selection of Appropriate Reactivity Scale

Oxides of nitrogen (NO_x) in the presence of oxygen forms ozone due to a series of photochemical reactions, with NO as an intermediate compound. The ozone formed is removed by rapid reaction with NO, thus keeping ozone levels insignificant. However, the presence of VOCs in the atmosphere either consumes the intermediate NO or converts it to NO₂. As such, once released into the atmosphere, VOCs have the potential to form ozone in the presence of NO_x [6]. The effect of VOC on ozone formation can be quantified in many different ways, but probably the most direct quantitative measure for practical air quality impact assessments is its "incremental reactivity". This is defined as the amount of additional ozone formation resulting from the addition of a small amount of the compound to the system in which ozone is formed, divided by the amount of the compound added [7]. Such an approach ascertains that no changes are made in the system due to addition of VOC. Incremental reactivity is considered as a product of two factors called as the "kinetic" and the "mechanistic" reactivities [8].

$$\text{Incremental Reactivity} = \text{Kinetic Reactivity} \times \text{Mechanistic Reactivity} \quad (4)$$

The kinetic reactivity is the fraction of the emitted VOCs which react

$$\text{Kinetic Reactivity} = \frac{\text{Fraction Reacted} = \text{VOC Reacted}}{\text{VOC Emitted}} \quad (5)$$

The mechanistic reactivity is the amount of ozone formed relative to the amount of VOCs which react

$$\text{Mechanistic Reactivity} = \frac{\text{Ozone Formed}}{\text{VOC Reacted}} \quad (6)$$

The value of incremental reactivity for a particular VOC is not absolute; it rather depends on concentration of different gases present in the system. Under high NO_x conditions with low VOC/NO_x ratio, VOCs have the maximum value of their incremental reactivity known as Maximum Incremental Reactivity (MIR). Under such conditions, the ozone formation is highly sensitive to changes in VOC concentration. On the other hand, under low NO_x conditions the ozone formation is primarily controlled by atmospheric NO_x. In such circumstances, Maximum Ozone Reactivity (MOR) provides a better estimation of the impact of VOC on ozone formation. In this study MIR scale developed by Carter [9] was used to determine OFP of emissions from HDDE. This MIR scale was used namely because compared to other reactivity scales and models, extensive experimental, theoretical and computational work has been done in creating this scale and this scale contains MIR values for the maximum number of VOCs.

3. Experimental Equipment and Procedure

The testing was done on 3 diesel engines retrofitted with and without passive catalyzed particulate filters. The engines were tested on Transportable Chassis Dynamometer and a sampling system was used to get data of organic compounds, inorganic compounds, individual elements, and particulate matter. The diesel engines were tested with the original exhaust system and subsequently fitted with DPFs: Johnson Matthey (CRTTM) and Engelhard (DPXTM), Fig. 1. Engines with after-treatment devices were tested on back-to-back cycles with single sets of media filter to ensure an adequate amount of particulate matter was collected during testing.

3.1 Test Fuels

Diesel engines were tested using a representative certified California Air Resources Board diesel fuel, named (CARB) and two ultra-low sulfur diesel fuels named (DF1 and DF2). These fuels enabled the retrofit and operation of after-treatment devices. The original DF1 formulation had 4.1 ppm (parts per million) sulfur, 8.9% aromatics by volume, and a cetane number of 65.3.

The high cetane and low aromatic levels have a negligible effect on DPF regeneration and conversion efficiency [10]. A second generation ULSD fuel named DF2 was formulated, recognizing that the sulfur content is the primary fuel property that must be controlled to enable the use of a catalyzed DPF. Like DF1, DF2 had a maximum sulfur content of 15 ppm but had aromatic and cetane levels that are more typical of today's diesel fuels. Some of the properties of the test fuels used are listed in Table 1.

Since this study focused on the OFP of the None Methane Hydrocarbons (NMHC) and carbonyls, the collection and analysis methods of only these compounds were applied. All measurements were done in accordance with procedures outlined in US Environmental Protection Agency (EPA) Code of Federal Regulations (CFR) Title 40 Part 86 Subpart N where applicable [6]. Detailed description of sampling train and procedures is available elsewhere [10, 11, 12]. Fig.1 represents testing setup for engine equipped with Engelhard particulate filter.

3.2 Data Collection Overview

During the engine emissions testing, at least three runs were performed for each test sequence, to ensure repeatable results, collecting the constituents for each sampling train. For calculation purpose, the hours of test runs were converted into distance based on test cycle depicting "real world vehicle cycle" for typical City Suburban Heavy Vehicle Route (CSHVR).

Table 1: Diesel Fuel Properties [11]

Diesel Fuel Property	CARB	DF1	DF2
Sulfur, ppm	114.5	4.1	12.7
Cetane Number	51.4	65.3	51.9
SFC Aromatics			
Total, mass %	16.1	7.7	17.5
PNA, mass %	3.78	1.68	4.07
FIA Aromatics			
Aromatics, vol. %	20.0	8.9	18.1
Olefins, vol. %	1.7	1.7	1.6
Saturates, vol. %	78.3	89.4	80.3
Heat of Combustion			
Net, BTU/lb	19,626	19,964	19,720
Gross, BTU/lb	18,383	18,649	18,468
Elemental Analysis			
Carbon, mass %	85.85	86.01	85.82
Hydrogen, mass %	13.63	14.42	13.72
Oxygen, mass %	0.52	<0.01	0.46
API Gravity	36.0	42.5	39.2
Density, g/ml @ 15°C	0.8437	0.8120	0.8286



Fig. 1 Engelhard DPXTM retrofitted test engine

The resulting distance specific mass emissions milligrams per mile (mg/mi) were obtained by simply dividing the integrated mass by the total distance "traveled" for that test:

$$\text{VOC} = \text{VOCmass} / \text{Distance} \quad (7)$$

To perform a comparison of the distance specific OFP for each combination, the MIR for each compound was multiplied by the emission rate of that compound. The summation of these products gave the distance specific OFP for a particular fuel exhaust after-treatment device combination.

$$mg_{oz}/mi = \sum [(mg_{Compound}) (MIR)] \quad (8)$$

Where, mg_{oz} is mass (in milligrams) of ozone, and $mg_{Compound}$ is the mass of VOC or carbonyl (in milligrams).

In addition to distance specific OFP, mass specific OFP (mg of ozone/mg of VOC) was also calculated for VOCs to investigate the effect of various after-treatment devices and fuels on the profile of diesel exhaust emissions. This was done by dividing distance specific OFP by distance specific emissions.

$$mg_{oz}/mg_{VOC} = (mg_{oz}/mi) / (mg_{VOC}/mi) \quad (9)$$

Where, mg_{oz} is mass (in milligrams) of ozone, and mg_{VOC} is the mass of volatile hydrocarbons (in milligrams).

4. Summary of Results

In the following summary, the distance specific emissions OFP are mentioned simply as emissions and OFP and reported in mg/mile and $mg_{oz}/mile$ respectively. The term "total emissions" imply sum of VOC emissions and carbonyl emissions. Similarly, the term "total OFP" imply sum of VOC OFP and carbonyl OFP. The use of phrases such as "CARB", "DF1", "DF2", imply use of respective fuel. Similarly, the use of phrases such as "DPX" and "CRT", imply that the engine was retrofitted with the respective after-treatment device, or "None" for not-retrofitted with such. Summary of diesel engine types, and summarized total emissions are represented in Table 2. Total emission reduction percentages mg/mi and mg_{oz}/mi was calculated relative to the total baseline fuel CARB's emissions measured on engine without after-treatment device.

Table 2: Summarized VOC and Carbonyl Emissions, and Total OFP test results.

Engine Model Navistar 530E, 8.7 liter, 6 cylinder, 275 horse power, 5 speed transmission					
Emissions Type and %Reduction	CARB + None	DF1 +None	DF1+ DPX	DF2 + None	DF2+ DPX
VOC mg/mi	71.26	55.36	10.98	71.02	15.53
Carbonyl mg/mi	66.91	73.36	0.34	83.67	0.38
Total mg/mi	138.17	128.72	11.32	154.69	15.91
Total OFP mg_{oz}/mi	923.79	891.57	43.95	921.05	55.77
% Reduction mg/mi		6.8	91.8	-12	99.89
OFP% Reduction mg_{oz}/mi		3.5	95.2	0.3	99.94
Engine Model Detroit Diesel Series 60, 12.7 liter, 6 cylinder, 470 horse power, 10 speed transmission					
Emissions Type and %Reduction	CARB + None	DF2 +None	DF1+ CRT	DF2+ CRT	DF2+ DPX
VOC mg/mi	63.95	79.60	24.86	34.47	35.94
Carbonyl mg/mi	72.55	88.45	0.22	0.73	0.32
Total mg/mi	135.50	168.05	25.08	35.20	36.26
Total OFP mg_{oz}/mi	970.48	126.09	111.07	138.00	140.00
%Reduction mg/mi		-2.4	81.5	74	73.2
OFP% Reduction mg_{oz}/mi		87	98.90	85.8	85.6
Engine Model Detroit Diesel Series 50, 8.5 liter, 4 cylinder, 275 horse power, 5 speed transmission					
Emissions Type and %Reduction	CARB + None	DF1 +None	DF2 + None	DF1+ CRT	DF2+ CRT
VOC mg/mi	44.53	28.97	37.14	7.63	8.79
Carbonyl mg/mi	45.61	22.62	27.58	0.22	0.40
Total mg/mi	90.14	51.59	64.72	7.85	9.20
Total OFP mg_{oz}/mi	587.75	403.61	416.95	33.86	39.29
%Reduction mg/mi		42.8	28.2	91.3	89.8
OFP% Reduction mg_{oz}/mi		31.3	29.1	94.2	93.3

It should be noted that since limited number of engines were tested during the study, any inferences about average emission factors representing the performance of a particular fuel or after-treatment device would be inappropriate. Having said that, this study gives some idea about the effect of fuel and after-treatment device on ozone forming potential. Exhaust emissions strongly depend on the combustion chemistry, and how the organic compounds oxidize in an after-treatment device. Any detailed discussion and investigation of the chemistry that governs the composition of exhaust emissions was out of scope of this study.

5. Conclusion

The objective of this study was to determine the effect of ULSD fuels and after-treatment devices on the ozone forming potential of heavy-duty diesel engines. The following may be concluded:

1. With identical DPF retrofitted on the engines, one of the ULSD fuel (DF1) performed better than the other DF2 by creating 15% to 22% less ozone impact.
2. Without any DPF retrofitted on the engine, the ozone impact of exhaust emission from the engine running on ULSD fuels was similar to that of baseline certification fuel (CARB).
3. Engines fueled by ULSD fuels and retrofitted with a DPF reduced the VOC emissions and VOC Ozone Forming Potential by up to 80% and 90% respectively as compared to the baseline.
4. Due to significant reduction in VOCs and carbonyls in the exhaust emissions from HDDE by the use of ULSD fuel and DPF, the total emissions and total OFP were reduced to less than 10% of baseline.
5. VOC emissions from vehicles retrofitted with a DPF and running on ULSD fuel had 20% to 40% less mass-specific VOC OFP as compared to the baseline.
6. The study showed that without any after-treatment device, the reactivity of emissions from engines running on ultra-low sulfur diesel fuels was similar to baseline engines, which were operating on CARB certified diesel fuel containing 114.5 parts per million sulfur (ppm S). When the engine was equipped with and operated on ULSD fuel, the ozone forming potential was reduced by approximately 95%. Reductions of up to 40% were observed on a mass-specific basis that is in terms of mass of ozone per mass of VOCs.

In summary, retrofitting heavy duty off-road diesel engine with a diesel particulate filter and running on an ultra-low-sulfur fuel significantly reduced volatile organic compound emissions, mass-specific volatile organic compounds and total ozone forming potentials of emissions per hours run or miles of distance.

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