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What Are Diesel Emissions

Diesel engines convert the chemical energy contained in diesel fuel into mechanical power. Diesel fuel is injected under pressure into the engine cylinder where it mixes with air and combustion occurs. The exhaust gases that are discharged from the engine contain several constituents that are harmful to human health and to the environment. Table 1 lists typical output ranges of the basic toxic material in diesel exhaust. Lower values can be found in new, clean diesel engines, while the higher values are characteristic for older equipment.

Table 1. Emissions from Diesel Engine

<table>
<thead>
<tr>
<th></th>
<th>CO</th>
<th>HC</th>
<th>DPM</th>
<th>NOx</th>
<th>SO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>vppm</td>
<td>vppm</td>
<td>g/m³</td>
<td>vppm</td>
<td>vppm</td>
<td>vppm</td>
</tr>
<tr>
<td>5 to 1,500</td>
<td>20 to 400</td>
<td>0.1 to 0.25</td>
<td>50 to 2,500</td>
<td>10 to 150</td>
<td></td>
</tr>
</tbody>
</table>

*Carbon monoxide (CO), hydrocarbons (HC), and aldehydes* are generated in the exhaust as the result of incomplete combustion of fuel. A significant portion of exhaust hydrocarbons are also derived from the engine lube oil. When engines operate in enclosed spaces, such as underground mines, buildings under construction, tunnels or warehouses, carbon monoxide can accumulate in the ambient atmosphere and cause headaches, dizziness and lethargy. Under the same conditions, hydrocarbons and aldehydes can cause eye irritation and a choking sensation. Hydrocarbons and aldehydes are major contributors to the characteristic smell of diesel exhaust. Hydrocarbons have also a negative environmental impact, being an important component of smog.

*Nitrogen oxides (NOx)* are generated from nitrogen and oxygen under the high pressure and temperature conditions in the engine cylinder. NOx consists mostly of nitric oxide (NO) and a few percent of nitrogen dioxide (NO2). Nitrogen dioxide is very toxic. NOx emissions are also a serious environmental concern because of their role in smog formation.

*Sulfur dioxide (SO2)* is generated from sulfur present in diesel fuel. The concentration of SO2 in the exhaust gas depends on the sulfur content of the fuel. Low sulfur fuels of less than 0.05% sulfur are being introduced for most diesel engine applications throughout the US and Canada. Sulfur dioxide is a colorless toxic gas with a characteristic, irritating odor. Oxidation of sulfur dioxide produces sulfur trioxide which is the precursor of sulfuric acid which, in turn, is responsible for the sulfate particulate matter emissions. Sulfur oxides have a profound impact on the environment being the major cause of acid rains.

*Diesel particulate matter (DPM)*, as defined by EPA regulations and sampling procedures, is a complex aggregate of solid and liquid material. Its origin is carbonaceous particles generated in the engine cylinder during combustion. The primary carbon particles form larger agglomerates and combine with several other, both organic and inorganic, components of diesel exhaust. Generally, DPM is divided into three basic fractions (Figure 1):

- **Solids** – dry carbon particles, commonly known as soot,
- **SOF** (*Soluble Organic Fraction*) – heavy hydrocarbons adsorbed and condensed on the carbon particles,
- **SO4** – sulfate fraction, hydrated sulfuric acid.
The actual composition of DPM will depend on the particular engine and its load and speed conditions. “Wet” particulates can contain up to 60% of the hydrocarbon fraction (SOF), while “dry” particulates are comprised mostly of dry carbon. The amount of sulfates is directly related to the sulfur content of the diesel fuel.

Diesel particulates are very fine. The primary (nuclei) carbon particles have a diameter of 0.01 - 0.08 microns, while the agglomerated particles diameter is in the 0.08 to 1 micron range. As such, diesel particulate matter is almost totally respirable and has a significant health impact on humans. It has been classified by several government agencies as either “human carcinogen” or “probable human carcinogen”. It is also known to increase the risk of heart and respiratory diseases.

Polynuclear Aromatic Hydrocarbons (PAH) are hydrocarbons containing two or more benzene rings. Many compounds in this class are known human carcinogens. PAHs in diesel exhaust are split between gas and particulate phases. The most harmful compounds of four and five rings are present in the organic fraction of DPM (SOF).
How Emissions Are Regulated

Regulations related to emissions and air quality may be divided into two classes:

• “tailpipe” emission regulations
• ambient air quality standards.

All diesel engines for highway applications and some for off-road use are subject to the “tailpipe” emission regulations. These regulations specify the maximum amount of pollutants allowed in exhaust gases from a diesel engine. The emissions are measured over an engine test cycle which is also specified in the regulations. The duty to comply is on the equipment (engine) manufacturer. All equipment has to be emission certified before being released to the market. The authorities regulating engine tailpipe emissions include the US EPA (Environmental Protection Agency) and California ARB (Air Resources Board). An example of this class of regulations is the EPA requirement that diesel particulate matter emissions from all heavy-duty diesel engines for highway use are below 0.1 g/bhp-hr.

Many applications of diesel engines in confined spaces are regulated through ambient air quality standards rather than by tailpipe regulations. The ambient air quality standards specify the maximum concentrations of air contaminants, known as Threshold Limit Values (TLV) or Permissible Exposure Limits (PEL), which are allowed in the workplace. These regulations are set and enforced by occupational health and safety authorities such as OSHA (Occupational Health and Safety Administration) or MSHA (Mining Safety and Health Administration). The duty to comply is on the end-user (mine operator, warehouse operator, etc.) who has to make sure that emission control measures which have been employed are adequate for the type and number of polluting equipment. A trade-off between several emission control methods is always possible. For example, the use of exhaust aftertreatment devices allows for a lower ventilation rate in the building. The final choice of emission control strategy can be, thus, dictated by economics.

The exact Threshold Level Values of particular air contaminants vary between different jurisdictions. TLV values for diesel exhaust pollutants, based on the ACGIH (American Conference of Governmental Industrial Hygienists) guidelines for 1993-1994, are listed in Table 2.

Table 2. Threshold Limit Values for Diesel Exhaust Pollutants

<table>
<thead>
<tr>
<th>Substance</th>
<th>TWA(^1)</th>
<th>STEL(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ppm</td>
<td>mg/m(^3)</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>25</td>
<td>29</td>
</tr>
<tr>
<td>Nitric Oxide</td>
<td>25</td>
<td>31</td>
</tr>
<tr>
<td>Nitrogen Dioxide</td>
<td>3</td>
<td>5.6</td>
</tr>
<tr>
<td>Formaldehyde(^3)</td>
<td>0.3(^4)</td>
<td>0.37(^4)</td>
</tr>
<tr>
<td>Sulfur Dioxide</td>
<td>2</td>
<td>5.2</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Diesel Particulates</td>
<td>-</td>
<td>0.15(^5)</td>
</tr>
</tbody>
</table>

\(^1\) Time-Weighted Average for a normal 8-hour workday.  \(^2\) Short-Term Exposure Limit, defined as a 15-minute TWA.  \(^3\) Suspected human carcinogen (A2).  \(^4\) Ceiling TLV.  \(^5\) ACGIH Notice of Intended Changes for 1995-1996, suspected human carcinogen (A2).
Diesel Oxidation Catalyst

The modern catalytic converter consists of a monolith honeycomb substrate coated with platinum group metal catalyst, packaged in a stainless steel container. The honeycomb structure with many small parallel channels presents a high catalytic contact area for the exhaust gases. As the hot gases contact the catalyst, several exhaust pollutants are converted into harmless substances: carbon dioxide and water.

![Figure 2. Catalytic Conversion of Carbon Monoxide and Hydrocarbons](image)

The diesel oxidation catalyst is designed to oxidize carbon monoxide, gas phase hydrocarbons, and the SOF fraction of diesel particulate matter to CO₂ and H₂O:

\[
CO + \frac{1}{2} O_2 \rightarrow CO_2
\]

\[
[\text{Hydrocarbons}] + O_2 \rightarrow CO_2 + H_2O
\]

\[
[SOF] + O_2 \rightarrow CO_2 + H_2O
\]

Diesel exhaust contains a sufficient amount of the oxygen necessary for the above reactions. Concentrations of O₂ in exhaust gases from a diesel engine vary between 3 and 17%, depending on the engine load. Typical conversion efficiencies for CO and HC in the GPS diesel catalyst are shown in Figure 2. The catalyst activity increases with temperature. A minimum exhaust temperature of about 200°C is necessary for the catalyst to “light off”. At elevated temperatures, conversions depend on the catalyst size and design and can be higher than 90%.
Conversion of diesel particulate matter is an important function of the modern diesel oxidation catalyst. The catalyst exhibits a very high activity in the oxidation of the organic fraction (SOF) of diesel particulates. Conversion of SOF may reach and exceed 80%. At lower temperatures, say 300°C, the total DPM conversion is usually between 30 and 50% (Figure 3). At high temperatures, above 400°C, a counterproductive process may occur in the catalyst. It is the oxidation of sulfur dioxide to sulfur trioxide, which combines with water forming sulfuric acid:

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 \xrightarrow{H_2O} H_2SO_4$$

Figure 3. Catalytic Conversion of DPM

Formation of the sulfate (SO₄) particulates occurs, outweighing the benefit of the SOF reduction. Figure 3 shows an example situation, where at 450°C the engine-out and the catalyst total DPM emissions are equal. In reality the generation of sulfates strongly depends on the sulfur content of the fuel as well as on the catalyst formulation. It is possible to decrease DPM emissions with a catalyst even at high temperatures, provided suitable catalyst formulation and good quality fuels of low sulfur content are used. On the other hand, diesel oxidation catalysts used with high sulfur fuel will increase the total DPM output at higher temperatures. This is why diesel catalysts become more widespread only after the commercial introduction of low sulfur diesel fuel.

The complex chemistry of diesel exhaust constituents requires that each emission problem is evaluated and analyzed individually to provide an appropriate catalyst. GPS works closely with customers to offer state-of-the-art solutions for their applications.
Hydrocarbon Traps

Diesel engines are characterized by relatively low exhaust gas temperatures. When diesel engines operate at idle or with low engine load, the catalyst temperature may be lower than required for catalytic conversion. At such conditions, the exhaust pollutants may pass untreated through the catalytic converter.

A new diesel catalyst technology has been developed to enhance the low temperature performance of the diesel oxidation catalyst. This technology incorporates hydrocarbon trapping materials into the catalyst washcoat. Zeolites, also known as molecular sieves, are most frequently used as the hydrocarbon trap. These zeolites trap and store diesel exhaust hydrocarbons during periods of low exhaust temperature, such as during engine idling. Then, when the exhaust temperature increases, the hydrocarbons are released from the washcoat and are oxidized on the catalyst. Due to this hydrocarbon trapping mechanism, the catalyst exhibits low HC light-off temperatures (Figure 4) and excellent diesel odor control.

![Hydrocarbon Conversion](chart.png)

**Figure 4. Catalyst with Hydrocarbon Trap**

GPS offers the hydrocarbon trap technology in its D-Series diesel catalysts. All GPS’ D-Series catalysts incorporate zeolites in their washcoat. They are capable of 40-50% HC conversion and effective diesel odor control at very low exhaust temperatures.

The HC trapping catalysts are designed to work at transient engine conditions. Since the low temperature performance occurs through adsorption rather than through catalytic conversion, periods of hot exhaust temperature are needed for hydrocarbons desorption and regeneration of the catalyst. Otherwise, the adsorption capacity will become saturated and increasing HC emissions will pass through the catalyst. The amount of zeolites in the GPS D-Series catalysts are sufficient for effective low temperature HC and odor control for a period of 15-30 minutes, before the trap saturates.

GPS offers several D-Series catalyst coatings which are engineered for different applications. D-Series catalysts incorporating sulfate suppressants for good high temperature DPM conversion are available.
Catalyst Construction

M-Series Diesel Oxidation Catalyst
The M-Series line of GPS’ diesel exhaust catalytic converters utilizes metallic monolith catalyst supports. The supports are made from a corrugated, high temperature stainless steel foil. Packages of several foil layers are fitted in stainless steel housings and secured in place by stainless steel rings. A special herringbone foil corrugation pattern creates a mixed flow cell structure. Exhaust gases are forced into the turbulent flow regime resulting in better contact between gas and catalyst, enhanced mass-transfer conditions, and higher conversion efficiency. Selected physical properties of GPS’ metallic monoliths are listed in Table 3.

The catalyst is deposited onto the foil prior to forming the substrate. A special foil washcoating process provides unequalled control of washcoat uniformity, adhesion, and efficient catalyst use. Thick washcoat concentrations in cell corners, which are inherent for other designs of metallic substrates, completely disappear with the precoated foil technology.

<table>
<thead>
<tr>
<th>Table 3. Physical Properties of GPS’ Catalyst Monoliths (uncoated)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metallic (M-Series)</strong></td>
</tr>
<tr>
<td>Cell Density, cpsi</td>
</tr>
<tr>
<td>Wall Thickness, mm</td>
</tr>
<tr>
<td>Geometric Surface Area, cm(^2)/cm(^3)</td>
</tr>
<tr>
<td>Open Frontal Area, %</td>
</tr>
<tr>
<td>Bulk Density, g/cm(^3)</td>
</tr>
</tbody>
</table>

D-Series Catalyst
The D-Series catalysts are available on ceramic substrates. Round cordierite substrates with square cell geometry is used in all D-series catalysts. Selected properties of the substrates are listed in Table 3.

Catalyzed substrates are wrapped in a special packaging mat and canned into a steel container using the tourniquet packaging technology. Tourniquet is known as the best catalytic converter canning technology, producing the most rugged and durable converters.

Ceramic substrates produce somewhat higher pressure drops than metallic substrates of the same dimensions, due to their thicker walls. However, for most applications, the D-series catalysts are sized larger than standard oxidation catalysts, in order to provide sufficient volume of the HC trap. By using D-series catalyst substrates of larger diameter and larger frontal area, it is possible to achieve comparable pressure losses when the standard catalyst and the D-series catalyst are installed on the same engine.

Most pressure drop comparisons between the ceramic and metal catalyst supports are based on bare (uncoated) substrates. While the uncoated ceramic supports do have thicker walls (Table 3), the difference in wall thickness decreases after the catalyst coating is applied. This is explained by the inherent porosity of ceramic substrates, which “soak in” a portion of the catalyst coating into the wall pores. Since metallic substrates are not porous, the entire catalyst coating stays at their surface. Therefore, when the same loading of
catalyst material is applied to a ceramic and a metallic substrate, it produces a thicker coating layer and more flow restriction in the metallic support.

**GPS’ Catalytic Converters**

Several advantages of GPS’ catalytic converters make them the superior choice as a generic, retrofit converter for heavy-duty applications:

- **High mechanical durability.** Metallic substrates will not crack or disintegrate even under harsh operating conditions and offer the best thermal durability. The ceramic substrates are canned using tourniquet technology, which produces the most rugged and durable catalytic converters.

- **Easy Maintenance.** The cell densities of the catalytic monoliths are carefully selected for each application. There is very little risk of clogging by diesel particulates. Most applications are virtually maintenance-free.

- **Low Pressure Drop.** Due to thin walls and large frontal area, the catalyst substrates have low pressure drops and do not cause any fuel penalty.

**Catalyst Durability**

The rugged construction of GPS’ diesel exhaust catalytic converters, using either metallic or ceramic supports, provides excellent mechanical durability. The catalyst substrate is designed to last for the entire life span of the engine. Good engine maintenance is necessary to sustain the catalyst activity for a similar period of time. There are two major causes of catalyst deactivation: (1) **high temperature** and (2) **poisoning**.

GPS’ catalysts may suffer thermal degradation when exposed to temperatures above 650°C (1200°F) for prolonged periods of time. Diesel engines have intrinsically cool exhaust gases and thermal catalyst deterioration is not likely to take place under normal operating conditions. Catalyst overheating may occur only as a result of serious engine malfunction, such as leaking injectors, when unburned fuel is oxidized in the catalyst and excessive temperature rise is observed due to the exothermic reaction.

Several chemical elements have the ability to either selectively poison the catalyst or to mask the catalytic surface, thus, preventing the contact between exhaust gases and active catalyst sites. Substances to be avoided include phosphorus, zinc, heavy metals, lead, arsenic, vanadium and silicone. Some of these elements (e.g., phosphorus) may be contained as additives in the engine lube oil. Low lube oil consumption and the use of low-phosphorus oils are guidelines for extended catalyst life. Leaks of lube oil into the exhaust system are very detrimental and can irreversibly deactivate the catalyst within a few hours or days.
Universal-Fit Designs and Available Sizes

Catalytic Converter Applications
For applications where a direct-fit catalytic muffler is not required or desired, universal-fit catalytic converters are available. These in-stock, ready-to-ship products are available in a variety of sizes and with a range of inlet/outlet pipe diameters. Installation is not as easy as with direct-fit products but simply involves cutting-out a section of the equipment’s exhaust pipe and installing the catalytic converter in its place. The section of exhaust pipe chosen must be straight with sufficient clearance on all sides and be located upstream of the muffler.

Converter Design
GPS offers two basic designs of universal-fit diesel catalytic converters, as shown in Figure 5 and Figure 6. The \textit{welded design} is more compact and is recommended for space limited applications. The \textit{clamped design} allows for easy removal of the center body for inspection and cleaning.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figures.png}
\caption{Figure 5. Welded Design}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figures.png}
\caption{Figure 6. Clamped Design}
\end{figure}

M-Series Diesel Oxidation Catalyst
The M-Series diesel oxidation catalyst yields a balance of high hydrocarbon, carbon monoxide, and particulate matter (SOF) conversions with low sulfate formation.

Standard dimensions of GPS’ M-Series catalytic converters are listed in Table 4.

\begin{table}[h]
\centering
\begin{tabular}{lcccccccccc}
\hline
Model & MD15 & MD25 & MD35 & MD55 & MD65 & MD85 & MD125 & MD155 & MD215 & MD295 & MD385 & MD665 \\
\hline
  inches & 6.9 & 7.8 & 8.4 & 9.3 & 9.8 & 10.2 & 10.8 & 12.3 & 17.2 & 17.2 & 17.2 & 17.2 \\
B, mm & 220 & 244 & 267 & 281 & 320 & 457 & 457 & 508 & 508 & 508 & 508 & 508 \\
  inches & 8.7 & 9.6 & 10.5 & 11.1 & 12.6 & 18.0 & 18.0 & 20.0 & 20.0 & 20.0 & 20.0 & 20.0 \\
  inches & 4.7 & 5.6 & 6.6 & 7.7 & 8.6 & 8.6 & 8.6 & 8.6 & 8.6 & 8.6 & 8.6 & 8.6 \\
D, mm & 65 & 79 & 91 & 111 & 130 & 141 & 167 & 192 & 225 & 263 & 301 & 379 \\
  inches & 2.6 & 3.1 & 3.6 & 4.4 & 5.1 & 5.6 & 6.6 & 7.6 & 8.9 & 10.4 & 11.8 & 14.9 \\
E (ID) & As per customer specifications \\
\hline
\end{tabular}
\caption{Dimensional Data for GPS’ M-Series Diesel Catalytic Converters}
\end{table}

Other models/sizes are available
D-Series Diesel Oxidation Catalyst

The D-Series diesel oxidation catalyst includes zeolite-based hydrocarbon traps for excellent low temperature activity and diesel odor control. This catalyst can also include sulfate suppressants which makes it suitable for heavy-duty applications.

Standard dimensions of GPS’ D-Series catalytic converters are listed in Table 5.

Table 5. Dimensional Data for GPS’ D-Series Diesel Catalytic Converters

<table>
<thead>
<tr>
<th>Model</th>
<th>DL42</th>
<th>DL62</th>
<th>DL102</th>
<th>DL152</th>
<th>DH222</th>
<th>DH312</th>
<th>DH422</th>
<th>DH522</th>
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</thead>
<tbody>
<tr>
<td>A, mm</td>
<td>267</td>
<td>280</td>
<td>325</td>
<td>325</td>
<td>356</td>
<td>406</td>
<td>498</td>
<td>518</td>
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<tr>
<td>inches</td>
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<td>12.8</td>
<td>14.0</td>
<td>16.0</td>
<td>19.6</td>
<td>20.4</td>
</tr>
<tr>
<td>B, mm</td>
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<td>335</td>
<td>382</td>
<td>432</td>
<td>513</td>
<td>533</td>
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<td>inches</td>
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<td>13.2</td>
<td>13.2</td>
<td>15.0</td>
<td>17.0</td>
<td>20.2</td>
<td>21.0</td>
<td></td>
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<tr>
<td>C, mm</td>
<td>142</td>
<td>168</td>
<td>185</td>
<td>220</td>
<td>220</td>
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</tr>
<tr>
<td>inches</td>
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<td>7.25</td>
<td>8.7</td>
<td>8.7</td>
<td>8.7</td>
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<td></td>
</tr>
<tr>
<td>D, mm</td>
<td>86</td>
<td>102</td>
<td>127</td>
<td>152</td>
<td>203</td>
<td>203</td>
<td>254</td>
<td>282</td>
</tr>
<tr>
<td>inches</td>
<td>3.4</td>
<td>4.0</td>
<td>5.0</td>
<td>6.0</td>
<td>8.0</td>
<td>8.0</td>
<td>10.0</td>
<td>11.1</td>
</tr>
</tbody>
</table>

E (ID) As per customer specifications

Other models/sizes are available

Direct-Fit & Custom Exhaust Aftertreatment Systems

Direct-Fit Catalytic Mufflers

GPS has direct-fit catalytic mufflers available for hundreds of models of construction equipment, mining equipment, forklift trucks and other diesel powered equipment. The pre-designed models are in-stock or can be built and shipped within a few days. Catalytic mufflers are available to replace the original muffler for any LPG, CNG, gasoline or diesel application. The emission control catalyst is built into the muffler and is selected based on the size of the engine. Catalytic mufflers are guaranteed to be an exact-fit replacement for the original muffler. The emissions reduction performance of catalytic mufflers is also guaranteed provided the engine is well maintained and no excessive CO emissions are present.

Global Plasma Solutions has a corporate policy of continuous product development. Specifications are subject to change without notice.