

Diesel Aerosols and Gases in Underground Mines: Guide to Exposure Assessment and Control





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Diesel Aerosols and Gases in Underground Mines: Guide to Exposure Assessment and Control

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Acronyms and Abbreviations Used in This Guide

ACGIH American Conference of Governmental Industrial Hygienists

ΑI aluminum

Al₂TiO₅ aluminum titanate

ANSI American National Standards Institute

APF assigned protection factor American Petroleum Institute API

APR air-purifying respirator AQE Air Quality Estimator ASC ammonia slip catalyst ASR air-supplying respirator

ASTM International, originally known as American Society for ASTM

Testing and Materials

B5 biodiesel blend containing 5% biodiesel and 95% petroleum diesel B20

biodiesel blend containing 20% biodiesel and 80% petroleum

diesel

B99 biodiesel blend containing 99% biodiesel and 1% petroleum diesel

B100 neat biodiesel

BPT balance point temperature

BQ9000 National Biodiesel Accreditation Program standards

BSFC brake-specific fuel consumption

BTH 2,6-di-t-butyl-p-cresol

C carbon

CARB California Air Resources Board

Ce

CCRT™ catalyzed continuously regenerating trap (registered trademark of

Johnson Matthey PLC)

CCV closed crankcase ventilation

CDPF catalyzed diesel particulate filter systems

CFR Code of Federal Regulations

CH₄ methane

CJ4 API grade for low-ash lubricating oil

CO carbon monoxide CO_2 carbon dioxide Cr chromium

CRT™ continuously regenerating trap (registered trademark of Johnson

Matthey PLC)

Diesel Emissions Evaluation Program **DEEP**

DEF diesel exhaust fluid DFE disposable filter element

DHHS U.S.Department of Health and Human Services

DOC diesel oxidation catalyst DOE U.S. Department of Energy DPF diesel particulate filter
DPM diesel particulate matter

EC elemental carbon
ECM engine control module
ECU electronic control unit
EGR exhaust gas recirculation
EGS electrochemical gas sensor

EPA U.S. Environmental Protection Agency

FAME fatty acid methyl ester FBC fuel-borne catalyst

Fe iron

Fed.Reg. Federal Register

FID flame ionization detector

FOEN Swiss Federal Office of the Environment FTIR Fourier transform infrared (spectrometer)

H₂ hydrogen H₂O water

H₂S hydrogen sulfide HC hydrocarbon

H_XC_Y generic hydrocarbon compound

HC-SCR hydrocarbon selective catalyst reduction

HD heavy-duty He helium

HEI Health Effects Institute

HEPA high-efficiency particulate air HPCR high-pressure common rail

HR hazard ratio

HTDFE high-temperature disposable filter elements

ID identification (number)

IR infrared

ISO International Standards Organization

LD light-duty

LHD load-haul-dump (vehicle)

LLSP laser light scattering photometry

LNC lean NO_X catalyst LSD low-sulfur diesel

LTDFE low-temperature disposable filter elements

MERV Minimum Efficiency Reporting Value

Mg magnesium $Mg_2Al_4Si_5O_{18}$ cordierite

M/NM metal and nonmetal (mines)

Mo molybdenum

MSDS material safety and data sheet

MSHA U.S. Mine Safety and Health Administration

Mtb mycobacterium tuberculosis

 N_2 nitrogen N_2O nitrous oxide

NBAC National Biodiesel Accreditation Commission

NBB National Biodiesel Board NDIR nondispersive infrared

NH₃ ammonia (NH₂)₂CO urea

NIOSH National Institute for Occupational Safety and Health

No. 1-D light middle grade of diesel fuel in the U.S. No. 2-D middle grade of diesel fuel in the U.S. No. 4-D heavy middle grade of diesel fuel in the U.S.

NO nitric oxide
NO₂ nitrogen dioxide
NO_x nitric oxides

NPPTL National Personal Protective Technology Laboratory

NREL National Renewable Energy Laboratory

O₂ chemical formula for oxygen

OC organic carbon

OEM original equipment manufacturer

OSHA U.S. Occupational Safety and Health Administration PADEP Pennsylvania Department of Environmental Protection

PAH polycyclic aromatic hydrocarbon PAPR powered air-purifying respirator

Pd palladium

PDM personal dust monitor

PEL Personal Exposure Limit (OSHA)

PF partial filter
PI particulate index
PM particulate matter

PPE personal protective equipment

ppm parts per million

Pt platinum

REL Recommended Exposure Limit (NIOSH)

Rh rhodium

RME rapeseed methyl ester

RTD resistance temperature detector

S sulfur

SAE Society of Automotive Engineers SCR selective catalytic reduction

SCRT™ catalyzed continuously regenerating trap with selective catalyst

reduction (registered trademark of Johnson Matthey PLC)

Si silicon

SiC silicon carbide SM sintered metal

SME soy methyl ester (biodiesel)

SMF sintered metal filter

 SO_2 sulfur dioxide

SOF soluble organic fraction (of DPM)

Sr strontium

SUVA Swiss National Accident Insurance Organization

SVOC semivolatile organic compounds

temperature that exhaust gas exceed for 30% of operating time T_{30}

TB tuberculosis TC total carbon

TLV **ACGIH Threshold Limit Value**

TPM total particulate matter TWA time-weighted average ULSDF ultralow sulfur diesel fuel U.S. United States (of America)

V vanadium

 V_2O_5/TiO_2 vanadium oxide/titanium oxide wash-coat catalyst in SCR systems

Verminderung der Emissionen von Real-Dieselmotoren im VERT

Tunnelbau

(Curtailing Emissions from Diesel Engines in Tunnel Construction)

VGT variable geometry turbocharger VOC volatile organic compound

volatile organic fraction (of DPM) VOF WRAP Western Regional Air Partnership

West Virginia Diesel Equipment Commission WVDEC

Unit of Measure Abbreviations Used in this Guide

cfm cubic feet per minute

gram

g in² square inch liter per minute lpm kPa kilopascal mbar millibar mg milligram

mg/m³ milligram per cubic meter

pound-force per square inch gauge psig

coefficient of determination

µg/cm² microgram per square centimeter

μg/m³ microgram per cubic meter

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1 Introduction

Diesel engines are a major contributor to concentrations of submicron aerosols, CO, CO₂, NO_X, SO₂ and hydrocarbons (HC) in underground coal and metal/nonmetal mines. The extensive use of diesel-powered equipment in underground mines makes it challenging to control workers' exposure to submicron aerosols and noxious gases emitted by those engines. In order to protect workers, mines need to establish a comprehensive program based on a multifaceted and integrated approach. This program should include a concerted effort to:

- Curtail emissions of the diesel particulate matter (DPM) and toxic gases at the source;
- Control pollutants after they are released in the underground mine environment; and
- Use administrative controls to reduce exposures of underground miners to pollutants.

Many of the technologies and strategies available to the coal and metal/nonmetal underground mining industries to control exposures of underground miners to diesel pollutants are similar. However, the differences in the U.S. regulations limiting DPM exposures of miners in underground coal mines [66 Fed. Reg. 27864 (2001)¹] and metal/nonmetal mines [71 Fed. Reg. 28924 (2006)] have a major bearing on how those technologies and strategies are implemented. In underground coal mines, achieving compliance is based on implementing technologies developed to control DPM and gaseous emissions directly at their source and providing sufficient quantities of fresh air to dilute criteria gases emitted by diesel engines [61 Fed. Reg. 55411 (1996)]. In contrast, the metal/nonmetal performance-based regulations enforce personal exposure limits (PEL) and provide much more latitude in the selection of technologies and strategies to control miners' exposures to DPM and gases [MSHA 2008].

The effort to reduce the exposure of underground miners to diesel pollutants requires the involvement of several key departments of mining companies, including those responsible for health and safety, engine/vehicle/exhaust aftertreatment maintenance, mine ventilation, and production, as well as the departments responsible for acquiring vehicles, engines, exhaust aftertreatment systems, fuel, and lubricating oil. Due to the complexity of this problem and the involvement of personnel from various departments in an underground mine, a program coordinator is crucial to the success of diesel control programs [McGinn et al. 2004; Conard et al. 2006; Schnakenberg 2006; Mischler and Colinet 2009]. The program coordinator must have adequate knowledge of issues related to exposure to diesel aerosols and gases, as well as the authority to coordinate all the efforts throughout various mine departments. The program

.

¹ Federal Register. See Fed. Reg. in references

coordinator must build a team of qualified personnel and solicit genuine support from workers as well as from corporate and mine management.

The diesel pollutants control program plan and execution of this plan should be dynamic and based on information gathered through surveillance efforts. This surveillance should include gathering information on parameters pertinent to planning, execution, and coordination of the program (e.g., size of the diesel-powered fleet, role of diesel-powered equipment in the mining process, type of engine emissions, contribution of diesel-powered equipment to exposure of underground miners to DPM and criteria gases, quality of diesel fuel and lubricating oil, and ventilation supply and demand). Surveillance efforts should also help to identify and quantify the extent of the problem, identify and evaluate potential solutions, and identify and establish a hierarchy of potential solutions. The adopted solutions should be instituted and implemented in a manner that takes the costs and benefits into consideration. The surveillance efforts should be continued throughout the implementation phase of the program, and the results should be used to constantly re-evaluate the effectiveness of the program and adjust actions accordingly.

Establishing a hierarchy of solutions is critical to the success of a multifaceted diesel pollutants control program. Certain technologies and strategies have a greater chance of success if their implementation is preceded by implementation of the prerequisite solutions. For example, the first step in retrofitting exhaust aftertreatment control systems to existing vehicles or equipment is to implement an effective maintenance and fuel/lubricating-oil supply program. This will provide sufficient information on engine emissions, quality of fuel and lubricating-oil, and lubricating oil consumption to allow for adequate design and performance monitoring while avoiding damage to the aftertreatment device(s) due to sulfate or ash formation.

A relatively wide variety of technologies and methodologies is available to the underground mining industry to reduce exposures to DPM and toxic gases. Those that are effective in curtailing DPM and toxic gaseous emissions at their source are discussed in detail in Section 2 of this handbook. Correspondingly, a detailed description of effective technologies and strategies for controlling pollutants after they are released in the underground mine environment is provided in Section 3. The methods and tools for monitoring ambient concentrations and personal exposures of underground miners to diesel particulate matter and toxic gases are described in Section 4. Various administrative controls and practices available to the mining industry to reduce emissions and exposures to DPM and toxic gases are discussed in Section 5.

2 Source Control of Diesel Particulate Matter (DPM) and Gases

2.1 Formation and Composition of Harmful Diesel Engines Emissions

2.1.1 Diesel Particulate Matter (DPM)

Introduction

The U.S. Environmental Protection Agency (U.S. EPA) defines diesel particulate matter (DPM) as any material being emitted from a diesel engine that can be collected on a filter through cooled and diluted exhaust (with the filter temperature held below 52°C, 126°F) [EPA 2002a]. This definition generally corresponds with any solid matter emitted or any liquid matter which is emitted or adsorbed onto the surface of these solid particles. This largely includes four byproducts of diesel combustion: elemental carbon (EC), organic carbon (OC), ash, and sulfuric compounds. These substances will quickly combine to form DPM aerosols (see Figure 1).

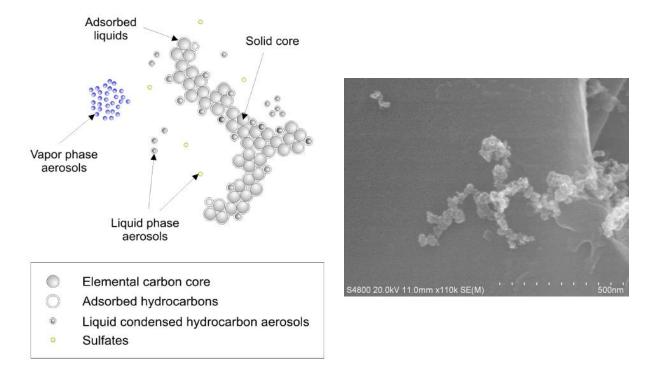


Figure 1. (left) A graphical depiction of the composition of diesel particulate matter and (right) a microscopic image of a typical diesel particle agglomerate.

Diesel particles are, in general, one order of magnitude smaller than other respirable dust aerosols in underground mines (typically less than one micron in size) [Kittelson 1998; Cantrell and Volkwein 2001]. Due to their small size, DPM aerosols behave similarly to the surrounding gases. They have much longer residence times in a mine atmosphere than larger mechanically generated particles, which are removed from the atmosphere quite quickly by gravitational settling. In addition, a large portion of diesel particles is deposited in the human respiratory tract in comparison to larger aerosols. These small diesel aerosols will

penetrate deeply into regions of the human lung where gas exchange occurs [Pietikäinen et al. 2009; Morawska et al. 2005], potentially increasing the health risks associated with long-term exposure to diesel aerosols. For these reasons, control of exposure to DPM particles is both an important and challenging task. The following section outlines the composition and formation of diesel particulate matter.

Elemental Carbon (EC)

Diesel engines function by allowing a mixture of fuel (a hydrocarbon, C_XH_Y) and intake air, which includes oxygen (O_2) , nitrogen (N_2) , and carbon dioxide (CO_2) , to ignite under high temperatures and pressures formed by compression [Diesel 1895]. This form of combustion allows overall cylinder conditions to be "lean"(fuel poor or oxygen rich), which promotes good efficiency and, as a result, a high conversion of fuel (C_XH_Y) into carbon dioxide (CO_2) and water vapor (H_2O) [Heywood 1988c]. However, fuel injection (typically used in diesel engines) also creates "rich" regions, or localized areas within the fuel injection plume that lack the amount of oxygen necessary for proper combustion of fuel. If temperatures are hot enough, fuel will burn without the presence of oxygen within these regions, creating charred remains, or solid carbon soot [EPA 2001a].

Another term for this soot is elemental carbon (EC). Once the EC is formed, most of it will combine with oxygen and burn during later stages of the combustion process [Kittelson et al. 1986; EPA 2001a; Kittelson 1998]. However, the remainder will be emitted from the engine exhaust as solid particulate matter, forming the core of a typical diesel-particle agglomerate. The formation of EC during combustion and expulsion is therefore driven by three primary factors: temperature, residence time, and availability of oxidants [EPA 2001a].

EC formation is reduced at the source by increasing the surface area contact of fuel and air during combustion so that the conversion rate of fuel into carbon dioxide and water vapor is high. This includes promoting lower local fuel/air ratios in contemporary engines through a number of in-cylinder controls (see Section 2.2.1) and using biodiesel fuels (see Section 2.3.1). Secondary reduction strategies for EC emissions involve capturing these particles within the exhaust system using diesel particulate filters (DPFs) (see Section 2.2.2.2).

Organic Carbon (OC)

On a mass basis, EC is the largest contributor to particulate matter (PM) emissions produced by a diesel engine [Noll et al. 2007]. Another large contributor is organic carbon (OC), or compounds that form when hydrocarbons (in fuel and lubricating oil) are consumed but not fully oxidized during the combustion process [Heywood 1988c]. Sources of OC emissions include fuel that is present in overly lean regions (where the ratio of fuel to air is too low to support efficient combustion), fuel that is post-injected ("leaked") into the chamber too late during the combustion process, or lubrication oil that is scraped from cylinder walls or introduced into the combustion chamber from other sources. In these instances, temperatures may be high enough to vaporize the hydrocarbons, but not high enough to convert them into carbon dioxide and water vapor.

OC compounds are partially composed of volatile material rather than nonreactive elemental carbon, and will react and change in both composition and phase during emission. If these

compounds are not in the gas phase, they are considered a component of DPM. Typically, this scenario occurs when organic compounds condense and adsorb onto the surface of larger EC particles, but they can also condense and form smaller nanoparticulates without the presence of EC [Kittelson 1998; Plumley 2005]. If OC remains in the gas phase, it is often referred to as an "HC" or "vapor-phase OC" emission, which is a pollutant that is regulated by the U.S. EPA. OC in the nongas phase is often referred to, by engine manufacturers, as the volatile organic fraction (VOF) or soluble organic fraction (SOF), depending on the measurement process used [Majewski and Khair 2006a]. It is important to note that, in the mining industry, the terms "organic carbon" or "OC" almost always refer to nongas-phase organics or to those substances that have mass and, therefore, contribute to total DPM mass.

Control of OC emissions at the source is accomplished by reducing oil consumption, improving fuel and oil formulations, and improving fuel injection design and timing (see Section 2.2.1). Diesel oxidation catalysts (DOCs) are often used within the exhaust system as a secondary control of OC emissions (see Section 2.2.2.1) [EPA 2007a; EPA 2004; Miller et al. 1997]. DPFs can also play a role in reducing OC emissions by capturing entire DPM particles, which may include adsorbed particle-bound OC (see section 2.2.2.2).

Ash

Fuel and lubricating oil often contain a number of additives (detergents, dispersants, etc.), which are composed of metallic elements. When these fluids are consumed during combustion, these metallic elements can form inorganic solids known as ash [Whitacre et al. 2010; Jung et al. 2003; Aravelli and Heibel 2007]. Normal wear of metallic engine components are another, though less substantial, source of ash generation. Although its contribution to DPM mass is often lower in comparison with other forms of particulate matter emissions [Kittelson 1998], ash cannot oxidize in secondary reactions with aftertreatment devices and may accumulate within the exhaust system and cause maintenance issues over time [Miller et al. 2007a; Vouitsis et al. 2007]. Reduction of ash formation can be accomplished by reducing the metallic fraction of the fuel and lube oil formulations, and by lowering the amount of oil consumed during the combustion process (see Section 2.3).

Sulfuric Compounds

Sulfur containing compounds is another contributor to DPM emissions. Sulfur dioxide, which forms when sulfur in the fuel and lubrication oil oxidizes during the combustion process [Kittelson et al. 2008; Whitacre et al. 2010; EPA 2004; Kittelson 1998], is a gaseous emission that can damage or deactivate expensive exhaust catalysts in contemporary diesel engines. During the emissions process, sulfur dioxide can react with other compounds in the exhaust and form solid sulfates, which contribute to overall DPM emissions. The transition toward ultralow sulfur diesel fuels (ULSDF) and low-sulfur content lubricants (e.g., CJ-4 oil, the newest API class) has promoted control over these emissions (see Section 2.3).

Total Carbon and EC:TC Ratio

Total carbon (TC) is a term used to describe the sum of the EC and OC fractions of DPM (TC = EC + OC). Likewise, the EC:TC ratio defines the fraction of EC in TC.

This relationship between EC and OC fractions depends on engine operating conditions, engine type, fuel type, and a number of other parameters. Because EC and OC make up over 80% of total DPM mass [Pierson and Brachaczek 1983; Kittelson 1998], the EC:TC ratio helps to quickly describe the general composition of DPM as well as the condition under which it was formed. For instance, if the EC:TC ratio is low, the aerosol contains more organic carbon and, if the source was a heavy-duty diesel engine fueled with a petroleum diesel fuel, it is likely that the DPM was formed under lower-load, lower-speed conditions, which is a typical operating mode approximation that corresponds with high OC formation.

2.1.2 Gases

Nitrogen Oxides (NO and NO₂)

At high temperatures, molecular nitrogen (N_2) from the intake air will react with oxygen (O_2) and hydrocarbons (HC) to form gaseous NO_X emissions, or oxides of nitrogen (NO and NO_2). During combustion, NO_X is formed in an area outside the fuel-rich region of the fuel plume where the proportion of fuel to air is optimal for efficient, high-temperature combustion [Dickey et al. 1998]. The rate of formation of NO_X is exponentially related to the temperature of combustion [Heywood 1988c]. Therefore, in-cylinder controls aimed at decreasing NO_X formation are almost always intended to lower the peak temperatures during the combustion process. In contemporary diesels, this is largely accomplished through exhaust gas recirculation (see Section 2.2.1) [Dickey et al. 1998]. Secondary control through various aftertreatment technologies, such as lean NO_X catalysts (LNCs) and selective catalyst reduction (SCR), may also be employed to further reduce NO_X emissions to acceptable levels (see Section 2.2.2.5 and Section 2.2.2.6).

NO_x/DPM Tradeoff

In conventional diesel combustion, almost any attempt to lower NO_X emissions through incylinder techniques results in an increase in DPM, and the converse is true as well. Referred to as the "NO_X/DPM" or "NO_X/PM" tradeoff, this correlation is controlled by the fact that NO_X formation increases at higher combustion temperatures and lean conditions, while DPM mass formation (driven by increased EC formation), will increase at lower combustion temperatures and rich conditions [Horibe and Ishiyama 2009; Heywood 1988c; Majewski and Khair 2006b; EPA 2001a; Helmantel and Golovitchev 2009; Kook et al. 2005]. Because of this correlation, it is very difficult to simultaneously reduce NO_X and DPM without combining various in-cylinder and aftertreatment technologies. For this reason, contemporary diesel-engine designs aimed at meeting U.S. EPA emissions regulations (which stipulate simultaneous reductions in NO_X and DPM emissions) have become particularly complex.

Carbon Monoxide

Carbon monoxide (CO) results from a non-ideal combustion. Its production is correlated to an incomplete oxidation of carbon in the fuel to carbon dioxide, most often from a lack of available oxygen or low gas temperatures. Therefore, under conditions which might produce locally fuel-rich mixtures, such as overloading and overfueling, diesel engines may produce higher concentrations of CO.

Compared to the CO emissions of a gasoline engine, the CO concentration in diesel exhaust is minimal due to the fact that diesel engines have a higher amount of available oxygen, or overall lean mixtures. Nevertheless, the extremely high toxicity related to human exposure to CO has prompted several regulatory agencies to limit the emission of CO from diesel engines [ACGIH 1991].

In diesel engines, reduction of CO emissions is achieved by improving the overall combustion efficiency by limiting any fuel-rich conditions within the cylinder (see Section 2.2.1) and using diesel oxidation catalysts (DOCs) within the exhaust system to convert CO to CO₂ in secondary reactions (see Section 2.2.2).

Gas-Phase Hydrocarbons (HC)

As a general guideline, hydrocarbons in the gas phase are typically referred to as volatile (VOC) and semivolatile organic compounds (SVOC). These are a complex mixture of many chemical species. Among them are polycyclic aromatic hydrocarbons (PAHs), which are widely investigated due to their toxicity. The formation of gas-phase hydrocarbons is outlined in Section 2.1.1. Likewise, control of gas-phase OC emissions at the source is accomplished in the same manner as nongaseous OC control—by reducing oil consumption, improving fuel and oil formulations, and improving fuel-injection design and timing (see Section 2.2.1). In addition, DOCs within the exhaust system are often used as a secondary control (see Section 2.2.2.1) [EPA 2007a; EPA 2004; Miller et al. 1997].

Sulfur Dioxide (SO₂)

As mentioned previously, sulfur dioxide forms when sulfur in the fuel and lubrication oil oxidizes during the combustion process [Kittelson et al. 2008; Whitacre et al. 2010; EPA 2004; Kittelson 1998]. This gaseous emission can damage or deactivate expensive exhaust catalysts in contemporary diesel engines. The transition toward ultralow sulfur diesel fuels (ULSDF) and low-sulfur content lubricants (CJ-4 oil) has promoted control over these emissions (see Section 2.3).

2.2 Engine Control Technologies

2.2.1 In-Cylinder Control Technologies

Introduction

In an effort to meet increasingly stringent worldwide emissions regulations, engine manufacturers have integrated a number of control technologies into new engine designs. Generally, these techniques are split into two categories: in-cylinder controls and aftertreatment. For the purposes of this manual, aftertreatment is defined as any technology that is incorporated into the exhaust system to physically or chemically alter or trap particulate and gaseous emissions (see Section 2.2.2). In-cylinder control technologies are designs or processes that are incorporated into the engine and its subsystems in an effort to prevent or manipulate the formation of unwanted emissions.

Mine operators have limited say in selecting in-cylinder controls because these technologies are usually incorporated during the design stage by the original equipment manufacturer (OEM). This is increasingly common in contemporary diesel engines intended to meet EPA nonroad emissions regulations [40 CFR 89*]. For this reason, the discussion on how incylinder control technologies can reduce mineworker exposure to diesel pollutants focuses on maintaining these technologies to the original OEM specifications and monitoring their performance rather than retrofitting or altering them. This is best accomplished through a stringent preventative maintenance program. This section provides an overview of the role in-cylinder controls play in emissions formation as well as suggested practices for maintaining the proper function of these technologies.

Technologies

Charge-Air Compression

Charge-air compressors (e.g., turbochargers and superchargers) allow more air to be introduced into the chamber before combustion, thus increasing the amount of fuel that can be injected and burned and, subsequently, enhancing the power output of the engine [Heywood 1988a; Majewski and Khair 2006c]. From an emissions perspective, the compression of charge air leads to leaner conditions within the cylinder during combustion (or situations where the fuel to air ratio is low), which promotes efficient, higher temperature oxidation of the fuel. Under these conditions, DPM formation is limited at the expense of increased NO_X gas emissions [Helmantel and Golovitchev 2009]. In addition, the compression of charge air may increase turbulence within the cylinder during induction, enhancing the mixing between fuel and air [Majewski and Khair 2006c] and further reducing DPM formation.

Charge-Air Cooling

The role of the intercooler is to combat the heating effects that charge compression systems have on intake air. Intercoolers decrease charge air temperature with minimal pressure loss.

^{*} Code of Federal Regulations. See CFR in references.

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