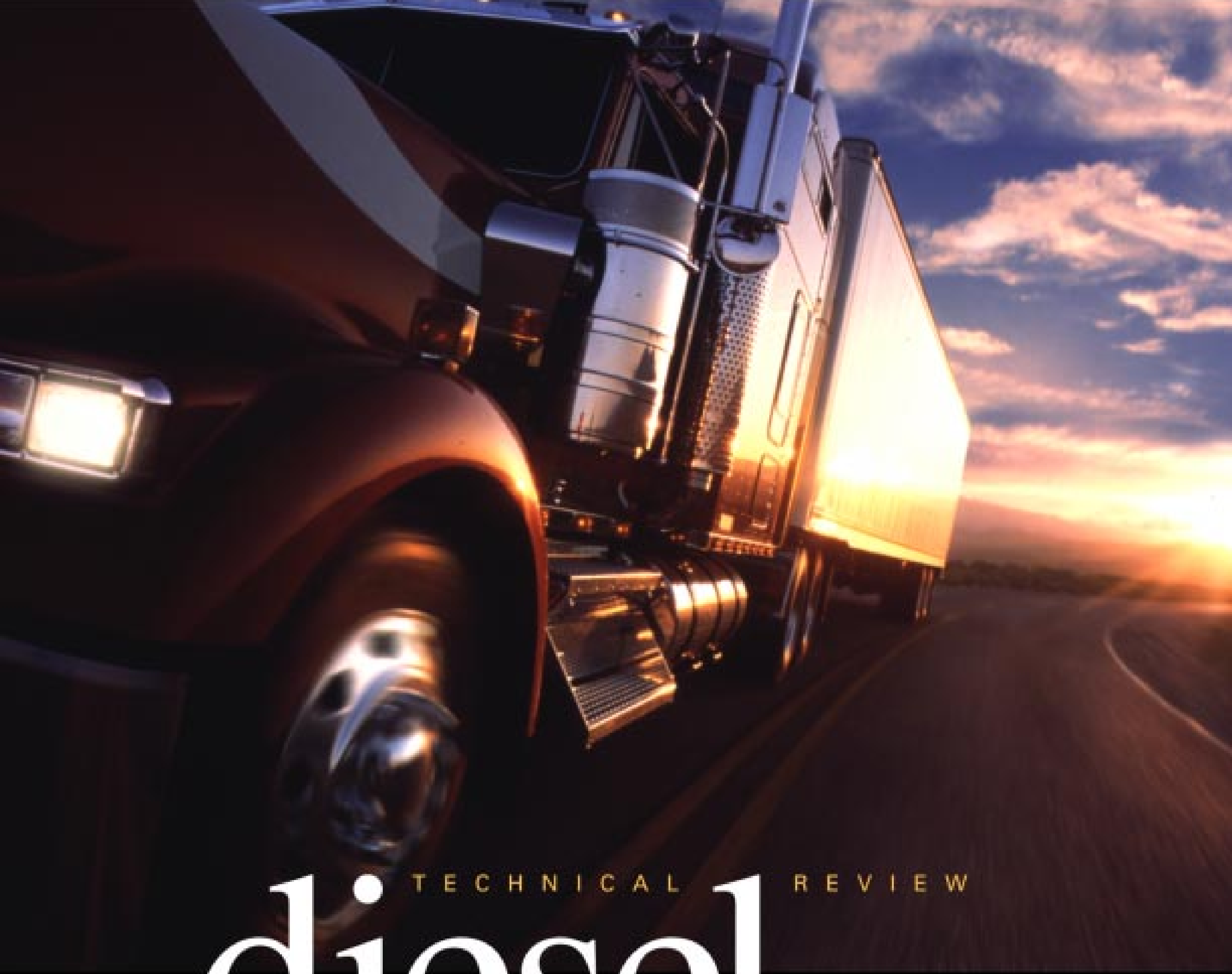

TECHNICAL REVIEW

diesel fuels

CHEVRON PRODUCTS COMPANY

Chevron

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Diesel Fuels Technical Review (FTR-2)

Introduction

The development of the internal combustion engine began in the late eighteenth century. Slow but steady progress was made over the next hundred years. By 1892, Rudolf Diesel received a patent for a compression ignition reciprocating engine. But his original design, which used coal dust as the fuel, didn't work.

Thirty-three years earlier, in 1859, crude oil had been discovered in Pennsylvania. The first product refined from crude was lamp oil *(kerosene)*. Since only a fraction of the crude made good lamp oil, refiners had to figure out what to do with the rest of the barrel.

Diesel, recognizing that the liquid petroleum by-products might be better engine fuels than coal dust, began to experiment with one of them. This fuel change, coupled with some mechanical design changes, resulted in a successful prototype engine in 1895. Today, both the engine and the fuel still bear his name.

The first commercial diesels were large engines operating at low speeds. They were used to power ships, trains, and industrial plants. By the 1930s, diesels also were powering trucks and buses. An effort in the late 30s to extend the engine's use to passenger cars was interrupted by World War II. After the war, the automotive diesel became very popular in Europe, but hasn't enjoyed comparable success in the United States.

Today, diesel engines are used worldwide for transportation, manufacture, power generation, construction, and farming. The types of diesel engines are as varied as their use – from small, high speed, indirect-injection engines to low speed direct-injection behemoths with cylinders three feet in diameter. Their success is due to their efficiency, economy, and reliability.

The subject of this *Review* is **diesel fuel** – its performance, properties, refining and testing. But because the engine and the fuel work together as a system, this *Review* devotes significant space to diesel engines, especially the heavy duty diesel engines used in trucks and buses. And because environmental regulations are so important to the industry, it examines their impact on both fuel and engine.

We hope that our readers, whatever their interest and background, will find this *Review* a source of valuable and accurate information about a product that helps keep America on the move.

Please note: This information is accurate as of Spring 1998. It may be superseded by new regulations or advances in fuel or engine technology.

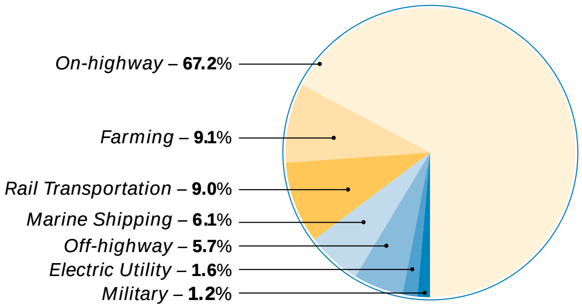
1 · Diesel Fuel Uses

Diesel fuel keeps the country moving. From consumer goods moved cross-country, to the generation of electric power, to increased efficiency on the nation's farms, diesel fuel plays a vital role in the nation's economy and standard of living. The major uses of diesel fuel are:

- on-road transportation
- farming
- rail transportation
- marine shipping
- off-road uses (mainly mining, construction, and logging)
- electric power generation
- military transportation

On-road[1] transportation, primarily trucks, accounts for two-thirds of the diesel fuel consumed in the United States *(see Figure 1-1)*. Because diesel fuel is used mainly to move goods from manufacturer to consumer, its sales are linked to the strength of the economy.[2] Sales of on-road diesel in the U.S. rose from 20 billion gallons in 1991 to more than 25 billion gallons in 1995, an increase of 5% to 6% a year *(see Figure 1-2)*. (In comparison, gasoline sales in 1995 were 119 billion gallons and jet fuel sales were 23 billion gallons.) Most of the diesel fuel sold in the U.S. is refined here. Relatively small volumes are imported and exported in response to market conditions in coastal or border locations.

Figure 1-1
1995 U.S. Diesel Fuel Sales[3]
38,053 million gallons



Comparable worldwide figures are not available. The International Energy Agency estimates the worldwide use of diesel fuel in 1994 was 187 billion gallons. However, this figure includes off-road use and some fuel oil uses. In Europe and Asia, where there is a significant population of diesel-powered automobiles, the use of diesel fuel nearly equals that of gasoline.

The term *diesel fuel* is generic; it refers to any fuel for a compression ignition engine. However, in

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[1] Instead of *on-road*, the U.S. EPA uses the term *on-highway* in their regulations and publications, but it includes vehicular traffic on all public roads, not just highways.

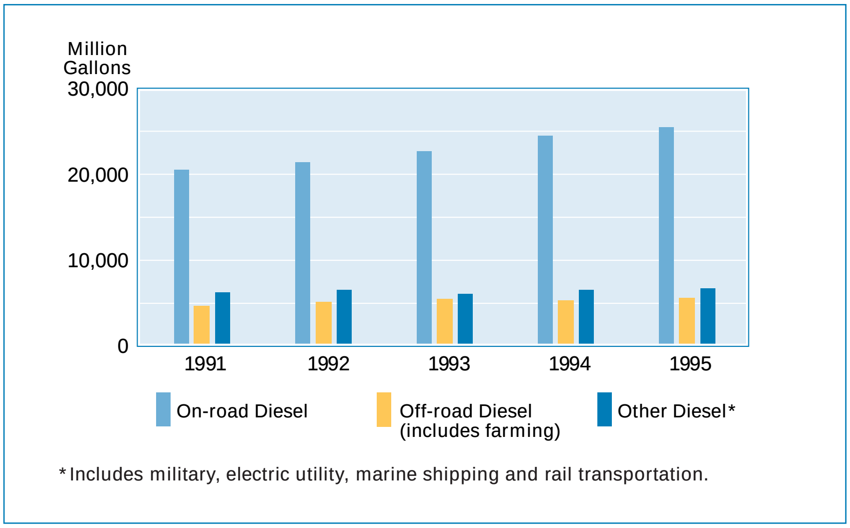
[2] *U.S. Highway Fuel Demand: Trends and Prospects,* American Petroleum Institute Research Study No. 084, November 1996.

[3] Source: DOE Energy Information Administration.

common use, it refers to the fuels made commercially for diesel-powered vehicles. In the United States, this is primarily Grade No. 2-D diesel fuel. However, two other grades, Grade No. 1-D and Grade No. 4-D, are also in commercial use. These grade designations are established by the American Society for Testing and Materials (ASTM). The grades are numbered in order of increasing density and viscosity, with No. 1-D the lightest and No. 4-D the heaviest *(see Chapter 5 for more information on diesel fuel specifications).*

Figure 1-2

Trends in U.S. Diesel Fuel Sales 1991 – 1995[4]



*Includes military, electric utility, marine shipping and rail transportation.

RELATED PRODUCTS

Some petroleum products have similar, but not identical, specifications and physical properties. For example, No. 2 fuel oil and No. 2-GT gas turbine fuel are similar to No. 2-D diesel fuel. And No. 1-GT gas turbine fuel oil, Jet A Aviation Turbine Fuel, and *kerosine*, the product specifically sold for use in lamps and stoves, are similar to No. 1-D diesel fuel.[5]

The specifications for each product are developed to ensure that it is suitable for the intended use. The fuel properties needed to keep a lamp burning are not nearly so stringent as those required to keep a jet aircraft aloft. Products with similar physical properties should not be used interchangeably without a complete understanding of the requirements of the intended use.

FUELS FOR MARINE DIESEL ENGINES

A variety of fuels are available for marine diesel engines. There is a set of four marine distillate fuels, some of which contain small amounts of *resid*,[6] and a set of 15 marine residual fuels in which resid is the majority constituent. Since resid increases viscosity, these fuels range in viscosity from less than one centistoke (cSt) to about 700 cSt at 122°F (50°C). The higher viscosity grades are preheated during use to bring their viscosity into the range suitable for marine diesel engine injection (8–27 cSt). Marine fuels also contain more sulfur than on-road diesel fuel. The maximum sulfur content specification varies from 1% to 5% mass for different grades.

Several organizations issue marine fuel specifications. Standard 8217 of the International Standards Organization (ISO) is the primary standard. ASTM maintains a parallel specification, D 2069.

The shipping industry increasingly prefers higher-viscosity residual fuels because they are less expensive. Although residual fuels don't burn as readily as distillate fuels, the slow speeds (60–200 rpm) of the large marine engines allow more time for combustion to occur.

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[4] Source: DOE Energy Information Administration.

[5] These four products represent a class of petroleum products with a boiling range of approximately 400°F to 600°F (200°C to 300°C). Following historical practice, this review will use the generic term *kerosene* to refer to this class of products and the petroleum distillate from which they are derived. However, the ASTM specification that defines the fuel for lamps and stoves is D 3699, *Standard Specification for Kerosine.* Dictionaries list the word as *kerosene*, with *kerosine* as an alternative spelling.

[6] *Resid* or *residuum* is the residue that remains when crude oil is distilled *(see page 21).*

2 · Diesel Fuel and Driving Performance

There are a number of engine performance characteristics that are generally recognized as important. Their relative importance depends on engine type and duty cycle (truck, passenger car, stationary generator, marine vessel, etc.).

- starting ease
- sufficient power
- low noise
- good fuel economy
- low wear (lubricity)
- low temperature operability
- long filter life (stability)
- low emissions

Engine design, by far and away, has the greatest impact on most of these characteristics. But since the focus of this publication is fuel, this chapter will discuss how they are affected by fuel properties.

STARTING

When a cold diesel engine is started *(cold start)*, the heat of compression is the only energy source available to heat the gas in the combustion chamber to a temperature that will initiate the spontaneous combustion of the fuel (about 750°F [400°C]). Since the walls of the combustion chamber are initially at ambient temperature rather than operating temperature, they are a significant heat sink rather than a heat source. And since cranking speed is slower than operating speed, compression is also slower, which allows more time for the compressed air to lose heat to the chamber walls. (A *glow plug* provides an additional source of heat in indirect-injection diesel engines.)

A fuel that combusts more readily will require less cranking to start an engine. Thus, if other conditions are equal, a higher *cetane number (see page 4)* fuel makes starting easier. As the compression temperature is reduced by variables like lower compression pressure, lower ambient temperature, and lower coolant temperature, an engine requires an increasingly higher cetane number fuel to start easily. Research indicates that fuels meeting the ASTM Standard Specification D 975 cetane number requirement of a minimum of 40 provide adequate cold starting performance in modern diesel engines. At temperatures below freezing, starting aids may be necessary regardless of the cetane number of the fuel.

Even after the engine has started, the temperatures in the combustion chamber may still be too low to induce complete combustion of the injected fuel. The resulting unburned and partially burned fuel is exhausted as a mist of small droplets that is seen as white smoke *(cold smoke)*. This situation normally lasts for less than a minute, but the exhaust is irritating to the eyes, and can be objectionable if a number of vehicles are started together in an enclosed space. A fuel with a higher cetane number can ameliorate the problem by shortening the time during which unburned fuel is emitted to the atmosphere.

POWER

Power is determined by engine design. Diesel engines are rated at the brake horsepower developed at the smoke limit.[1] For a given engine, varying fuel properties within the ASTM D 975 specification range *(see page 34)* does not alter power significantly. For example, in one study seven fuels with varying distillation profiles and aromatics contents were tested in three engines. In each engine, power at peak torque and at rated speed (at full load) for the seven fuels was relatively constant. However, if fuel viscosity is outside of the D 975 specification range, combustion may be poor, resulting in loss of power and fuel economy.

NOISE

The noise produced by a diesel engine is a combination of combustion noise and mechanical noise. Fuel properties can affect only combustion noise.

In a diesel engine, the fuel ignites spontaneously shortly after injection begins. During this delay, the fuel is vaporizing and mixing with the air in the combustion chamber. Combustion causes a rapid heat release and a rapid rise of combustion chamber pressure. The rapid pressure rise is responsible for the diesel *knock* that is very audible for some diesel engines.

Increasing the cetane number of the fuel can decrease the amount of knock by shortening the ignition delay. Less fuel has been injected by the time combustion begins and it has had less time to mix with air. As a result, the rapid pressure rise, along with the resulting sound wave, is smaller.

One design approach to reducing combustion noise is to shape the injection – setting the rate slow at first and then faster – to reduce the amount of fuel entering the cylinder during the ignition delay period. Another is to use indirect-injection *(see page 48)*.

FUEL ECONOMY

Here again, engine design is more important than fuel properties. However, for a given engine used for a particular duty, fuel economy is related to the heating value of the fuel. Since diesel fuel is sold by volume, fuel economy is customarily expressed as output per unit volume e.g., miles per gallon. Therefore, the relevant units for heating value are *heat per gallon (Btu per gallon)*. Heating value per gallon is directly proportional to density when other fuel properties are unchanged.

ASTM specifications limit how much the heating value of a particular fuel can be increased. Increasing density involves changing the fuel's chemistry – by

CETANE NUMBER

Cetane Number **is a measure of how readily the fuel starts to burn** ***(autoignites)*** **under diesel engine conditions. A fuel with a high cetane number starts to burn shortly after it is injected into the cylinder; it has a short** ***ignition delay period.*** **Conversely, a fuel with a low cetane number resists autoignition and has a longer ignition delay period.** ***(See page 41 for information about measuring cetane number.)***

Although the cetane number of a fuel is assumed to predict its ignition delay in any engine, the actual delay represented by the cetane number is valid only for the single cylinder engine in which it was measured. The fuel's performance in other engines may differ.

A fuel's ignition delay is determined by its chemistry. In a warm engine, the delay is independent of the physical characteristics of the fuel, like volatility and viscosity. (The cetane index correlations ***[see page 41]*** **utilize density and distillation temperature properties to estimate cetane number, but these properties are being used as indirect indicators of fuel chemistry, not as direct variables.)**

Cetane numbers apply only to distillate fuels; they are not measured for fuels containing petroleum resid (marine fuels).

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[1] In engine terminology, *brake horsepower* is the usable power delivered by the engine *(see sidebar, page 16)*. The *smoke limit* is the fuel-air ratio at which visible particulate emissions become excessive and are no longer acceptable.

changing aromatics content – or changing its distillation profile by raising the initial boiling point, the end point, or both. Increasing aromatics is limited by the cetane number requirement (aromatics have lower cetane numbers [*see page 28*]); changing the distillation profile is limited by the 90% distillation temperature requirement.

Combustion catalysts may be the most vigorously promoted diesel fuel aftermarket additive *(see page 56)*. However, the Southwest Research Institute, under the auspices of the U.S. Transportation Research Board, ran back-to-back tests of fuels with and without a variety of combustion catalysts. These tests showed that a catalyst usually made "almost no change in either fuel economy or exhaust soot levels."[2] While some combustion catalysts can reduce emissions, it is not surprising that they don't have a measurable impact on fuel economy. To be effective in improving fuel economy, a catalyst must cause the engine to burn fuel more completely. But there is not much room for improvement. With unadditized[3] fuel, diesel engine combustion efficiency is typically greater than 98%. Ongoing design improvements to reduce emissions are likely to make diesel engines even more efficient.

HEATING VALUE

The *heating value* (also referred to as *energy content*) of diesel fuel is its heat of combustion, the heat released when a known quantity of fuel is burned under specific conditions. In the U.S., the heating value is usually expressed as British thermal units (Btu) per pound or per gallon at 60°F. (International metric [SI] units are kilojoules per kilogram or per cubic meter at 15°C.) For *gross heating value,* the water produced by the combustion is recondensed to a liquid. For the lower *net heating value,* the water remains as a gas.

Since engines exhaust water as a gas, the net heating value is the appropriate value for comparing fuels. Heating value is customarily expressed *per unit volume,* specifically *Btu per gallon,* because customers buy fuel by volume.

WEAR

Lubricity Some moving parts of diesel fuel pumps and injectors are lubricated by the fuel. To avoid excessive wear, the fuel must have some minimum amount of *lubricity.* (Lubricity is the ability to reduce friction between solid surfaces in relative motion.) The lubrication mechanism is a combination of *hydrodynamic lubrication* and *boundary lubrication.*

In hydrodynamic lubrication, a layer of liquid prevents contact between the opposing surfaces. For diesel fuel pumps and injectors, the liquid is the fuel itself; and viscosity is the key fuel property. Fuels with higher viscosities will provide better hydrodynamic lubrication. However, diesel fuels with viscosities within the ASTM D 975 specification range provide adequate hydrodynamic lubrication.

When high load and/or low speed has squeezed out much of the liquid that provides hydrodynamic lubrication, boundary lubrication becomes important. Now, small areas of the opposing surfaces are in contact. Boundary lubricants are compounds that form a protective anti-wear layer by adhering to the solid surfaces.

Many diesel fuels are good boundary lubricants. This is not due to the hydrocarbons that constitute the bulk of the fuel. Instead it is attributed to trace amounts of oxygen- and nitrogen-containing compounds and certain classes of aromatic compounds. Evidence for the role of trace quantities is the fact that the lubricity of a fuel can be restored with the addition of as little as 10 ppm of an additive.

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[2] David S. Moulton and Norman R. Sefer, *Diesel Fuel Quality and Effects of Fuel Additives,* Transportation Research Board, Washington D.C., 1984, p. 23.

[3] Rather than repeatedly use the awkward phrase "addition of an additive," the petroleum industry has coined the word "additize."

Lubricity enhancing compounds are naturally present in diesel fuel derived from petroleum crude by distillation. They can be altered or changed by *hydrotreating,* the process used to reduce sulfur and aromatic contents. However, lowering sulfur or aromatics, per se, does ***not*** necessarily lower fuel lubricity.

The use of fuels with poor lubricity can increase fuel pump and injector wear and, at the extreme, cause catastrophic failure. Such failures occurred in Sweden in 1991, when two classes of “city” diesel with very low sulfur and aromatics contents were mandated. Heavy hydrotreating was necessary to make these fuels. The problem was solved by treating the fuel with a lubricity additive.

Many users were concerned when the U.S. Environmental Protection Agency (EPA) mandated on-road low sulfur (0.05% mass, maximum) diesel fuel and when California Air Resources Board (CARB) mandated low aromatics (10% volume, maximum) diesel. But there is no documented evidence that the use of these fuels, as a class, has led to increased wear, much less catastrophic failures.

Cleanliness Inadequate lubricity is not the only cause of wear in diesel engine fuel systems. Diesel fuel can cause abrasive wear of the fuel system and the piston rings if it is contaminated with abrasive inorganic particles. Fuel injectors and rotary distributor fuel pumps are particularly susceptible to wear because the high liquid pressures they generate require extremely close tolerances between parts moving relative to each other.

The ASTM diesel specification limits the ash content of most diesel fuels to 100 ppm, maximum. (Inorganic particles and oil soluble metalo-organic compounds both contribute to the ash content, but only inorganic particles will cause wear.) The U.S. Government has a tighter specification of 10 mg/L (approximately 12 ppm) for all particulate matter. Neither specification addresses particle size. While the fuel filters recommended by engine manufacturers have a nominal pore size of 10 microns,[4] studies by Southwest Research Institute reveal that the critical particle size for initiating significant abrasive wear in rotary injection fuel pumps and in high-pressure fuel injection systems is 6–7 microns.

Acidity Organic acids in diesel fuel also can cause corrosive wear of the fuel system. While this may be a significant wear mechanism for high sulfur diesel, it is less significant for low sulfur diesel because hydrotreating to reduce sulfur also destroys organic acids.

LOW TEMPERATURE OPERABILITY

Low temperature operability is an issue with middle distillate fuels because they contain straight and branched chain hydrocarbons *(paraffin waxes)* that become solid at ambient wintertime temperatures in colder geographic areas. When this happens, the wax may plug the fuel filter or it may completely gel the fuel, making it impossible for the fuel system to deliver fuel to the engine.

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[4] 1 micron = 1 micrometer = 10^{-6} meter.

Engine design changes to address this problem include locating the fuel pump and filter where they will receive the most heat from the engine. The practice of pumping more fuel to the injectors than the engine requires is also beneficial, since the warmed excess fuel is circulated back to the tank. While the primary purpose of this recycle is to cool the injectors, it also heats the fuel in the fuel tank.

Sometimes operators allow diesel equipment to idle in cold weather rather than turning the engine off when it is not in use. The cost of the fuel is less than the cost of winterizing the engine. However, vehicles designed for low temperature operation are usually equipped with heated fuel tanks, insulated fuel lines, and heated fuel filters.

In a refinery, there are a number of approaches to improve a fuel's low temperature operability:

- Manufacture it from less waxy crudes.
- Manufacture it to a lower end point. (This excludes higher boiling waxy components with higher melting points.)
- Dilute it with a fuel with a lower wax content (No. 1-D diesel fuel or kerosene).
- Treat it with a low temperature operability additive *(see page* 57*)*.

After the fuel is in the distribution system, dilution is the most practical way to lower cloud point. Additives are used to improve low temperature filterability and to lower pour point. When they work, additives have several advantages over dilution: they are available in all areas of the country; the treatment cost is less; and treatment doesn't lower fuel density and, thus, heating value and fuel economy.

Low temperature operability issues are also discussed on page 38. The tests to characterize a fuel's low temperature operability *(cloud point, pour point, cold filter plugging point [CFPP], and low temperature flow test [LTFT])* are discussed on page 44.

PARAFFIN WAX

All middle distillate fuels will precipitate paraffin wax when they are cooled to a low enough temperature. Paraffin wax is a solid mixture of crystalline hydrocarbons, primarily straight chain hydrocarbons, plus some branched chain and cyclic hydrocarbons *(see page 24).* When it is oil-free, this wax melts in the range 100°F to 180°F (40°C to 80°C). Paraffin wax occurs naturally in all crude oils; the amount depends on the specific crude oil(s) from which it was produced and on the processing used.

As fuel is cooled, it reaches a temperature at which it no longer is able to dissolve the waxy components, which then begin to precipitate out of solution. The temperature at which wax just begins to precipitate and the fuel becomes cloudy is the *cloud point* as measured by ASTM D 2500.

If the fuel is cooled below the cloud point, more wax precipitates. At approximately 6° to 10°F (3° to 5°C) below the cloud point (for fuels that do not contain a pour point depressant additive) the fuel becomes so thick it will no longer flow. This temperature is called the *pour point* or *gel point* as measured by ASTM D 97.

FILTER LIFE – FUEL STABILITY

Unstable diesel fuels can form soluble gums or insoluble organic particulates. Both gums and particulates may contribute to injector deposits and particulates can clog fuel filters. The formation of gums and particulates may occur gradually during long term storage, or quickly during fuel system recirculation due to fuel heating.

Storage stability of diesel fuel has been studied extensively because of governmental and military interest in fuel reserves. But storage stability is of little concern to the average user, since most diesel fuel is consumed within a few weeks of manufacture. Thermal stability, on the other hand, is a necessary requirement for diesel fuel to function effectively as a heat transfer fluid.

Thermal stability may become more important because diesel engine manufacturers expect future injector designs to employ higher pressures to achieve better combustion and lower emissions. The change will subject the fuel to higher temperatures and/or longer injector residence times.

Low sulfur diesel fuels tend to be more stable than their high sulfur predecessors, because hydrotreating to remove sulfur also tends to destroy the precursors of insoluble organic particulates *(see page 29)*. However, hydrotreating also tends to destroy naturally occurring antioxidants. It may be necessary for the refiner to treat some low sulfur diesels with a stabilizer to prevent the formation of peroxides that are the precursors of soluble gums.

EMISSIONS

The EPA has established emission standards for new engines *(see page 15)*. The regulated emissions are hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NO_X), and particulate matter (PM). Unlike gasoline powered engines, diesel engines don't have much trouble meeting the HC and CO standards. The standards for NO_X and PM are much more challenging. Some of the current emission reduction technologies are addressed in Chapter 6.

Emissions control is an aspect of performance in which fuel can make a difference. *(The effect of fuel properties on various emissions is discussed on page 16.)* Some fuel changes have already been mandated by regulatory agencies. In 1993, the EPA limited the sulfur content of diesel fuel for on-road use in order to reduce the emissions of PM and sulfur oxides (SO_X). In the same year, CARB expanded the limitation on sulfur content to diesel fuel for all vehicular use (including off-road vehicles), and added a limit on aromatics content, to reduce both PM and NO_X.

Diesel engines emit PM continuously. Usually the particles are too small and their concentration is too low for the PM to be visible. In contrast, visible black smoke in a diesel engine's exhaust indicates a problem. The root cause is the injection of too much fuel for the available air (too high a fuel-air ratio), resulting in incomplete combustion.

The fuel system of a diesel engine is designed and calibrated so it doesn't inject more fuel than can be consumed completely by the available air (the *smoke limit)*. There are U.S. standards for exhaust smoke from high-speed heavy duty engines. Beginning with the 1984 model year, the opacity of smoke may not exceed 20% during engine acceleration mode or 15% during engine lugging mode under specified standard test conditions.

Smoke after engine warmup is an indication of maintenance or adjustment problems. A restricted air filter may be limiting the amount of air, or a worn injector may be introducing too much fuel. Other causes are miscalibrated fuel pumps or maladjusted injection timing. Changes made to fuel pump calibration and injection timing to increase the power of an engine can lead to increased emissions.

Because smoke is an indication of mechanical problems, California and other states have programs to test the exhaust opacity of on-road heavy duty trucks under maximum engine speed conditions *(snap idle test).* Owners of trucks that fail the test are required to demonstrate that they have made repairs to correct the problem. There are also smoke regulations for ships in port.

Variation of most fuel properties within the normal ranges will not lead to the high level of PM represented by smoking. The exception is cetane number; fuel with a very high cetane number can cause smoking in some engines. The short ignition delay causes most of the fuel to be burned in the diffusion controlled phase of combustion *(see page 51)*, which can lead to higher PM emissions.

Fuel can indirectly lead to smoking by degrading injector performance over time, when:

- Gums in the fuel are deposited on the injectors, causing sticking, which interferes with fuel metering.
- Petroleum resid or inorganic salts in the fuel result in injector tip deposits that prevent the injector from creating the desired fuel spray pattern. (Marine and some other large diesel engines are designed to burn fuel containing large amounts of petroleum resid.)
- Excessive abrasive contaminants or organic acids in the fuel, or inadequate fuel lubricity cause abrasive or corrosive injector wear.

3·Diesel Fuel and Air Quality

Today it is almost impossible to discuss motor vehicles without considering air quality. A number of areas in the United States fail to meet one or more federal air quality standards and in some of these areas, vehicles are responsible for a large part of the problem emissions.

This chapter explains who regulates emissions, and why and how. It also explains which emissions come from vehicles and how they are formed. Finally, it explains how emissions are affected by diesel fuel characteristics and how diesel fuel is being reformulated to reduce emissions.

The explanations are complicated because they involve complex regulations and complex science. Sometimes complete accuracy is sacrificed to keep this review as short and simple as possible. The number of acronyms is unavoidable; both government regulations and science use them heavily.

PROGRESS

Are the efforts of adding pollution control systems to vehicles and reformulating fuels paying off in better air quality? The answer is – *yes*. Urban air quality has improved steadily over the last twenty years. To illustrate, Figure 3-1 shows the trend lines for the concentrations of three air pollutants – ozone, carbon monoxide, and nitrogen dioxide – in the U.S. The fact that these decreases are not uniform from year to year may indicate the impact of meteorological fluctuations on ambient pollutant concentrations.

The improvement in urban air quality is due primarily to significant advances in emissions control technologies that have been applied to various emission sources. For example, today a new model heavy duty diesel truck emits only about 10% of the particulate matter and 27% of the nitrogen oxides emitted by a similar vehicle built before emission controls were established. Even greater improvements have been achieved for gasoline powered cars. Similarly impressive improvements have been achieved for certain stationary sources, such as refineries and power plants.

LEGISLATION

The Clean Air Act of 1963 initiated the federal government's regulation of air pollution. It was amended in 1967, 1970, 1977, and most recently, in 1990. The stated purpose of the act is: "… to protect and enhance the quality of the Nation's air resources." As the purpose suggests, the act addresses a wide range of air pollution issues, not just vehicle emissions.

THE BEGINNING

Smog is the common term for the forms of air pollution involving haze and oxidants such as ozone. Smog was identified as a serious problem in the Los Angeles Basin in the 1950s. As university scientists and government health scientists investigated the problem, they found that vehicle emissions were a significant source of smog precursors. Acting on this information, the California Legislature established emissions limits for 1966 model year cars and 1969 model year diesel trucks. As part of a greater air quality program, federal legislation to reduce vehicular emissions was initiated with the adoption of the Clean Air Act of 1963. The first federal limits for exhaust emissions from gasoline-powered vehicles were implemented starting with the 1968 model year and from diesel-powered vehicles starting with the 1971 model year.

ADMINISTRATION/REGULATION

In many cases, laws are not administered by the body that enacts them. Congress or a state legislature assigns the administrative responsibility to a governmental agency. The 1970 amendments of the Clean Air Act created the U.S. Environmental Protection Agency (EPA) and made it responsible for implementing the requirements of the act and its amendments. California's laws covering vehicle emissions are administered by the California Air Resources Board (CARB), which was established by the Legislature in 1969.

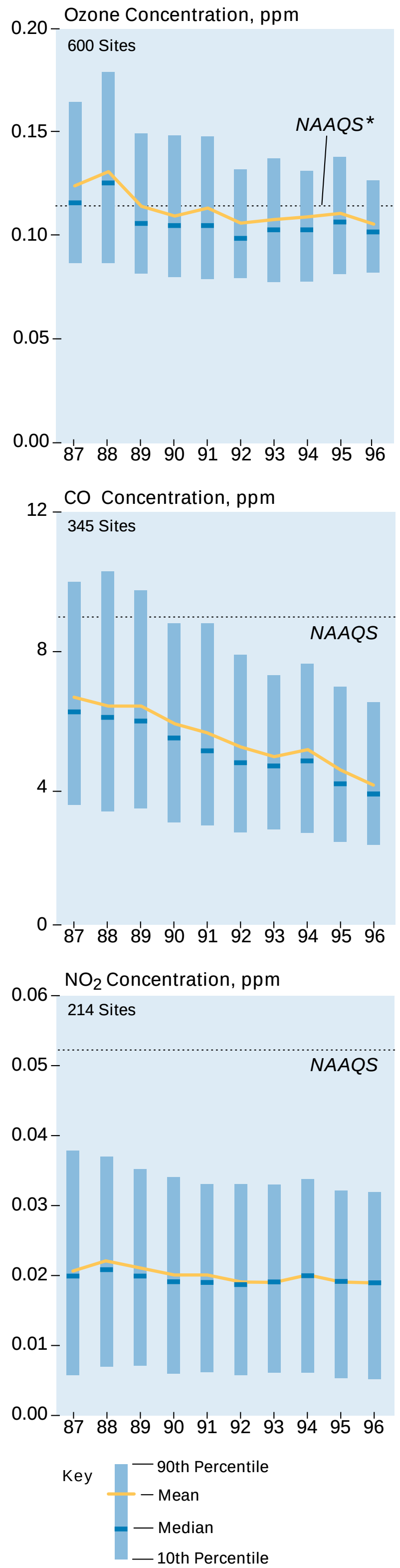
While some laws contain a lot of detail, they can't address all the issues surrounding their application in our complex industrial society. The agency administering the law has the responsibility to write regulations which will make the legislative intent a reality. Title 40 of the Code of Federal Regulations contains the EPA regulations for environmental protection.

As Congress intended, the states do much of the work to carry out the provisions of the Clean Air Act and its amendments. State and local air pollution agencies hold hearings, write regulations (based on guidance from the EPA), issue permits, monitor pollution, issue notices of violations, and levy fines. It is appropriate for the states to take the lead, because states and local agencies need to select and enforce the pollution control strategies that make sense for their region. Geography, weather conditions, housing patterns, regional traffic patterns, and the nature of local industry all influence pollution levels.[1]

The Clean Air Act and its amendments "… set deadlines for the EPA, states, local governments and businesses to reduce air pollution." Each state is required to develop a state implementation plan (SIP) that explains the actions it will take to meet or maintain the air quality standards set by the EPA. The EPA must approve each state's SIP. The EPA assists the states by providing scientific research, expert studies, engineering designs, and money to support clean air programs.

Figure 3-1

Pollutant Concentration Trends in the U.S. 1987–1996[2]



*National Ambient Air Quality Standard

AIR QUALITY STANDARDS

Air pollutants are natural and artificial airborne substances that are introduced into the environment in a concentration sufficient to have a measurable effect on humans, animals, vegetation, or building materials. From a regulatory standpoint, substances become air pollutants when the EPA says they are. As part of the regulatory process, the Clean Air Act requires the EPA to issue a *criteria document* for each pollutant documenting its adverse effects. Regulated pollutants are therefore referred to as *criteria pollutants.* The EPA uses the information in the criteria documents to set National Ambient Air Quality Standards (NAAQS) at levels that protect public health and welfare. Figure 3-2 lists the criteria pollutants and the federal and California standards. In most cases, the California standards are more stringent. Some of the criteria pollutants, like carbon monoxide, are primary pollutants, which are emitted

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[1] *The Plain English Guide to the Clean Air Act.* U.S. Environmental Protection Agency, EPA 400-K-93-001, April 1993.

[2] *National Air Quality and Emissions Trends Report.* U.S. EPA 454/R-97-013, 1996.

directly by identifiable sources. Others, like ozone, are secondary pollutants, which are formed by reactions in the atmosphere. And others, like particulates, are of mixed origin.

Figure 3-2
Ambient Air Quality Standards

Criteria Pollutant	Averaging Time	Maximum Average Concentration	
		Federal Standard	California Standard
Ozone (O_3), ppm	1-hour/8-hour	0.12/0.08*	0.09/–
Carbon Monoxide (CO), ppm	1-hour/8-hour	35/9	20/9.0
Nitrogen Dioxide (NO_2), ppm	1-hour/annual	–/0.053	0.025/–
Sulfur Dioxide (SO_2), ppm	1-hour/24-hour/annual	–/0.14/0.03	0.25/0.05/–
Suspended Particulate Matter (PM10), ug/m^3	24-hour/annual	150/50	50/30
Suspended Particulate Matter (PM2.5), ug/m^3	24-hour/annual	65/15*	–/–
Lead, ug/m^3	30-day/quarterly	–/1.5	1.5/–
Sulfates, ug/m^3	24-hour	–	25

* In July 1997, the EPA announced a new 8-hour ozone standard and new 24-hour and annual PM2.5 standards. Final details for implementing these standards are still being developed.

AIR POLLUTANTS

Ozone Ground-level ozone is formed by the interaction of volatile organic compounds (VOC),[3] oxides of nitrogen (NO_X), and sunlight.[4] The role of sunlight explains why the highest concentrations of ozone in the atmosphere occur in the summer months and why there is a diurnal pattern to the concentrations, with the highest concentrations occurring in the afternoon and lower concentrations at night.

"[Ozone] damages lung tissue, reduces lung function, and sensitizes the lungs to other irritants … [It is] responsible each year for agricultural crop yield loss in the U.S. of several billion dollars and causes noticeable [leaf] damage in many crops and species of trees."[5]

Volatile Organic Compounds VOCs are not a criteria pollutant, though some specific compounds are classified as toxics *(see page 14)*. Their importance stems from their role in forming ozone. All hydrocarbons in the atmosphere are considered VOCs, as are many other types of organic compounds. This explains

[3] EPA defines VOCs as all organic compounds that participate in atmospheric photochemical reactions. Since methane and ethane have negligible photochemical reactivity, EPA does not considered them VOCs for regulatory purposes.

[4] In the stratosphere, a layer of ozone partially shields the earth from solar ultra-violet radiation. Stratospheric ozone is formed by a different mechanism than ground-level ozone.

[5] *National Air Quality and Emissions Trends Report*, 1992. Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, EPA 454/R-93-031, October 1993.

why so much effort is directed toward reducing hydrocarbon emissions from vehicles and stationary sources.

The EPA estimates that, nationwide, about equal quantities of VOC emissions come from manmade and natural sources.[6] Diesel engines accounted for only about 5% of the manmade VOC emissions in 1996 *(see Figure 3-3).*

Not all hydrocarbons contribute equally to ozone formation. Their reactivity depends on their chemical structure and the atmospheric conditions to which they are subjected. Under most conditions, olefins and aromatics are more reactive than paraffins.

The toxicity of organics depends on their structure. Most hydrocarbons are nontoxic at low concentrations. Some low molecular weight aldehydes are carcinogenic and some monocyclic and polycyclic aromatic hydrocarbons (PAH) are suspected or known carcinogens.

Carbon Monoxide (CO) CO is generated primarily by combustion processes. The EPA estimates that diesel engines were responsible for about 5% of the manmade CO emissions in 1996 *(see Figure 3-4).* CO's toxicity stems from its ability to reduce the oxygen carrying capacity of blood by preferentially bonding to hemoglobin.

Nitrogen Dioxide (NO_2) The air quality standard applies only to NO_2, but where emissions are concerned, NO and NO_2 are usually analyzed simultaneously and expressed as NO_X. Most (94%) of the NO_X emissions are manmade. The EPA estimates that diesel engines generated about 27% of the manmade NO_X emissions in 1996 *(see Figure 3-5).*

While NO is nontoxic by itself, it contributes to ozone formation. "NO_2 can irritate the lungs and lower resistance to respiratory infection …"[6] In some locations, NO_X is also an important precursor to particulate matter.

Sulfur Dioxide (SO_2) SO_2 is produced primarily by the combustion of fuels containing sulfur. Facilities (stationary sources) that burn fuel oil and coal are the major source. On-road and off-road engine fuels are estimated to be the source of less than 3% of the total SO_2 emissions.

SO_2 is a moderate lung irritant. Along with NO_X, it is a major precursor to acidic deposition (acid rain).

Figure 3-3
Emissions Sources:
1996 National Manmade VOC Emissions[6]
19,086,000 short tons[7]

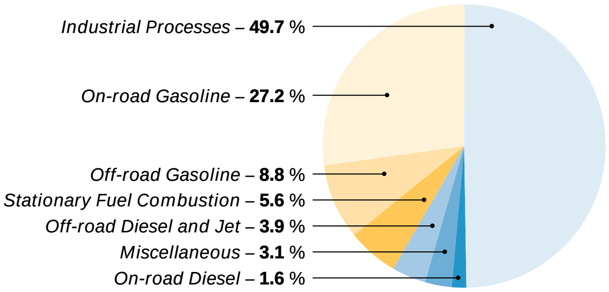


Figure 3-4
Emissions Sources:
1996 National Manmade Carbon Monoxide Emissions[6]
88,822,000 short tons

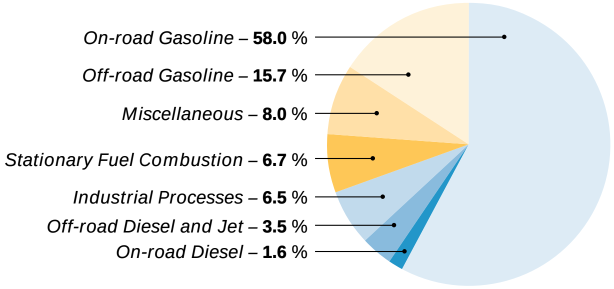
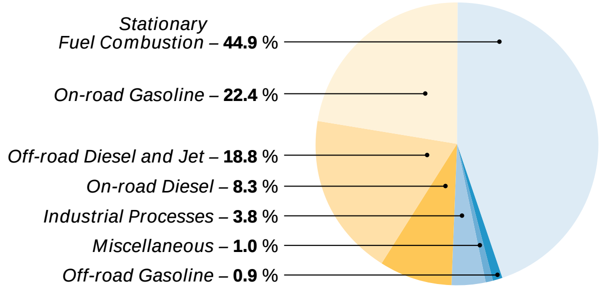


Figure 3-5
Emissions Sources:
1996 National Manmade Nitrogen Oxide Emissions[6]
23,393,000 short tons



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[6] *National Air Pollutant Emissions Trends Report,* 1900-1996. EPA 454/R-97-011, December 1997.

[7] 1 short ton = 2,000 pounds = 0.907 metric tons.

DIESEL EXHAUST TOXICITY

The potential of diesel exhaust to cause adverse health effects in people is controversial. However, several non-regulatory agencies have concluded that exposure to diesel exhaust increases the risk of lung cancer. The International Agency for Research on Cancer (IARC) concluded that the evidence for diesel exhaust as a cause of cancer was sufficient in animals, but limited in humans. As a result, they categorized diesel exhaust as a potential human carcinogen[8] (Category 2A). The National Institute of Occupational Safety and Health (NIOSH) reached the same conclusion, recommending that whole diesel exhaust be regarded as a potential cause of cancer. The EPA and the California EPA are currently reviewing the available data on diesel exhaust and are expected to finalize their conclusions in 1998.

Particulate Matter (PM10 and PM2.5) PM10 is particulate matter with a particle size less than or equal to 10 microns (0.0004 inch) and PM2.5 has a particle size less than or equal to 2.5 microns (0.0001 inch). The EPA estimates that fugitive dust from roads accounts for about two-thirds of the total PM10 nationwide. Less than 2% of PM10 is attributed to on-road and off-road engines, but the percentage is higher in urban areas where there is less dust and more combustion sources. Particulates from diesel engines include primary carbon particles and secondary sulfate and nitrate aerosols formed from SO_2 and NO_X.

After a review of scientific evidence of the health effects of particulate matter, the EPA recently established a new standard for PM2.5. The EPA found that while both coarse and fine particles can increase respiratory symptoms and impair breathing, fine particles are more likely to contribute to serious health effects. Most of the particulate emissions from diesel engines are smaller than 2.5 microns.

Air Toxics The toxic air pollutants listed by the Clean Air Act Amendments of 1990 included: benzene, polycyclic organic matter (POM),[9] acetaldehyde, formaldehyde, and 1,3-butadiene. Of this group, only POM is found in diesel fuel. Diesel exhaust contains POM and possibly trace amounts of the other toxic pollutants.

VEHICLE EMISSIONS: SOURCES

When hydrocarbon fuel is burned with the correct amount of air in a diesel engine, the gases that are left are predominately water vapor, carbon dioxide and nitrogen – all of which are benign, although carbon dioxide is a greenhouse gas. However deviations from this ideal combustion lead to the production of some VOCs, CO, NO_X, SO_2, and PM.

Diesel engines are substantial emitters of PM and NO_X, but only small emitters of CO and VOCs. Gasoline engines are the greatest emitters of CO and substantial emitters of VOCs and NO_X, but only modest emitters of PM.

Since diesel engines are designed to run lean, i.e., with excess oxygen, they do not emit much carbon monoxide or unburned hydrocarbons. And because diesel fuel has a much higher boiling range than gasoline (and consequently a much lower volatility), evaporative VOC emissions are not a problem.

Oxides of Nitrogen Air is 78% nitrogen by volume. Diesel engines mainly produce NO_X by “burning” a small amount of the nitrogen in the air drawn into the cylinder. At the high temperatures encountered in a diesel combustion chamber, the nitrogen combines with oxygen to form NO_X. The formation of NO_X becomes significant at about 2900°F (1600°C) and increases rapidly as the temperature rises above this threshold.

Any organic nitrogen in the fuel also contributes to NO_X emissions, but this source is miniscule compared to nitrogen in the air. Combustion chamber deposits increase NO_X emissions slightly. The deposits are believed to raise

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[8] IARC Monograph 46, 1989.

[9] Also called *polynuclear aromatics* (PNA) or *polycyclic aromatic hydrocarbons* (PAH).

the combustion temperature because they act as thermal insulators, reducing heat loss to the combustion chamber walls.

Particulate Matter PM emissions are mainly the result of the heterogeneous nature of diesel combustion. When fuel is injected into hot compressed air in the cylinder, regions develop that are fuel-rich and oxygen deficient. Because of the high temperature and pressure in the cylinder, the fuel may start to break down before it has a chance to mix with air and burn normally. These high temperature cracking reactions *(pyrolysis)* lead to the formation of carbonaceous soot particles. Unburned or partially burned fuel can condense on these particles, increasing their size and mass. Finally, these particles can stick together *(agglomerate)* to create visible smoke.

Diesel exhaust NO_X and PM are linked by the nature of diesel combustion. Efforts to reduce PM by increasing combustion efficiency lead to higher combustion temperatures and, thus, higher NO_X emissions. Lowering NO_X formation by lowering combustion temperature leads to less complete combustion and, thus, higher PM emissions.

VEHICLE EMISSIONS: LIMITS

The EPA set limits for emissions from heavy-duty diesel engines starting with the 1971 model year. A number of companies manufacture engines, but not vehicles. Also, the companies that manufacture vehicles may use engines from several different sources. To simplify the qualification process, the EPA elected to have emission standards apply to diesel *engines* rather than *vehicles.*

Figure 3-6 lists the EPA standards for heavy-duty highway engines. The EPA also has engine emission standards for diesel buses, off-road diesels, marine diesels, and railroad diesels. California sets its own limits on diesel emissions, which are generally the same as the federal standards, although sometimes slightly more restrictive.

Figure 3-6

Selected Federal Heavy-duty Highway Diesel Engine Emission Standards

Year	CO (g/bhp-hr)	HC (g/bhp-hr)	NO_X (g/bhp-hr)	PM (g/bhp-hr)
1990	15.5	1.3	6.0	0.60
1991-1993	15.5	1.3	5.0	0.25
1994-1997	15.5	1.3	5.0	0.10
1998+	15.5	1.3	4.0*	0.10**

* This standard had to be met by 1996 in California.

** Urban buses must meet a 0.05 g/bhp-hr PM standard.

Exhaust emissions are very dependent on how a vehicle is operated. To standardize the test conditions, the EPA requires that exhaust emissions be measured while the engine is operated according to a specified speed-time cycle on an engine dynamometer. The EPA Transient Test Procedure includes segments designed to mimic congested urban, uncongested urban, and freeway driving, along with both a cold start and a hot start.

VEHICLE EMISSIONS: FUTURE LIMITS

The EPA recently issued a rule setting emission standards for 2004 model year engines. Instead of having separate HC and NO_X categories, the new standard has a single non-methane hydrocarbons (NMHC) + NO_X category. Since NMHC and NO_X are of concern because they participate in the reactions that generate ozone, it makes sense to view them as one category rather than two. The limit for the combined category will be lowered to 2.4 grams per brake horsepower – hour (g/bhp-hr), or 2.5 g/bhp-hr with a limit of 0.5 g/bhp-hr on NMHC. This will reduce NO_X emissions from these engines by 50%, which the EPA expects will lead to lower ambient ozone concentrations.

The new rule also includes provisions to ensure that the engines retain these low emissions throughout their lifetime. The EPA and engine manufacturers plan to meet in 1999 to review progress toward this goal. Potential changes to fuel properties considered necessary to meet the new standards will be one of the topics.

Concern about carbon dioxide emissions and their relationship to global warming is leading to serious consideration of using diesel engines in light-duty trucks, vans, sport utility vehicles, and U.S. passenger cars. The inherent fuel efficiency of the diesel engine, relative to the gasoline engine, results in substantially lower emissions of CO_2 per mile. However, emissions control technology will need to advance for a new generation of diesel vehicles to meet EPA standards.

UNITS OF DIESEL ENGINE EMISSIONS

Brake horsepower **(bhp) is a unit of power. The adjective "brake" indicates that it is the power developed at the engine's drive shaft, which is less than the power developed inside the engine's cylinders. It is equal to the *indicated power,* delivered from the expanding combustion gas in the cylinder to the piston, minus all loses which include friction, pulling air into the engine, and driving engine accessories.**

Brake horsepower-hour **(bhp-hr) is a unit of work (energy); it is the work done when the engine's shaft exerts one horsepower for one hour. Expressing engine emissions as weight per unit of work (grams/brake horsepower-hour) allows the use of a single standard for engines of all sizes. A larger engine generates a higher volume of exhaust and a higher absolute amount of emissions than a smaller engine, but it also can do more work.**

The emissions of gasoline-powered vehicles also are expressed as weight per unit of work, but the units are *grams per mile.* There are two reasons why these units are not appropriate for diesel engines. First, as the text explains, diesel emissions standards apply to the engine, not to the vehicle. Since the engine is not tested in a vehicle, expressing the emissions *per mile* would require a number of assumptions. Second, there is much more variation in the sizes and loads of diesel vehicles than gasoline vehicles. Using *per mile* standards would penalize large trucks hauling heavy loads, even when they are more emissions-efficient.

VEHICLE EMISSIONS: DIESEL FUEL EFFECTS

Advances in engine design have produced very large reductions in NO_X and PM emissions since the EPA began setting emission standards for diesel engines in 1971. The composition of diesel fuel has had much less influence on emissions, but reformulated diesel fuels have played a small role in achieving needed emissions reductions. The most important fuel parameters in this regard are:

Sulfur The sulfur content of diesel fuel affects PM emissions because some of the sulfur in the fuel is converted to sulfate particles in the exhaust. The fraction converted to PM varies from one engine to another, but reducing sulfur decreases PM linearly in almost all engines. For this reason, the EPA limits the sulfur content of on-road diesel fuel (low sulfur diesel fuel) to 0.05% mass[10] (500 ppm) maximum and CARB applies the same limit to all vehicular diesel fuel (on-road and off-road). As a result, the national average

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[10] When percent is used to express one element's relationship to the whole, the value depends on the units of quantity that are used. Percent by mass (% mass) compares the mass of one element to the mass of the whole; percent by volume (% volume or % vol) compares the volume of one element to the volume of the whole.

sulfur content for low sulfur diesel fuel is between 300 and 350 ppm. At a sulfur level of 300 ppm, sulfate particles comprise about 10% of total PM emissions for an engine emitting 0.1 g PM/bhp-hr.

Cetane Number Increasing the cetane number improves fuel combustion and tends to reduce NO_X and PM emissions. NO_X seems to be reduced in all engines, while PM10 reductions are more engine-dependent. These cetane number effects also tend to be non-linear in the sense that increasing the cetane number does the most good when starting with a relatively low cetane number fuel.

Density Changes in fuel density affect the energy content of the fuel brought into the engine at a given injector setting. European studies[11] indicate that reducing fuel density tends to decrease NO_X emissions in older technology engines that cannot compensate for this change. Emissions from modern engines, with electronic injection and computer control, appear to be independent of density.

Aromatics Reducing the aromatics content of diesel fuel reduces NO_X and PM10 in some engines. Recent European studies[11] indicate that polynuclear-aromatics content is key to the reduction, and that the concentration of single-ring aromatics is not a factor.

Volatility T_{95} is the temperature at which 95% of a particular diesel fuel distills in a standardized distillation test (ASTM D 86). Reducing T_{95} decreases NO_X emissions slightly, but increases hydrocarbon and CO emissions. PM10 emissions are unaffected.[11]

REFORMULATED DIESEL FUEL

The first environmental regulations governing diesel fuel composition took effect in 1985 in southern California. CARB limited the sulfur content to 0.05% mass because of that region's severe air quality problems.

In October 1993, separate regulations from EPA and CARB took effect. The EPA set a maximum sulfur content of 0.05% mass for on-road diesel fuel, nationwide. CARB applied this same limit to both off-road and on-road (vehicular) diesel fuel. In the other states, the limit on the sulfur content of off-road fuel is the ASTM D 975 limit of 0.5% mass for high sulfur No. 2-D diesel fuel.

CARB also limited the aromatics content of vehicular diesel fuel to 10% volume maximum. Alternative formulations with higher aromatics contents are allowed if they have been demonstrated to achieve the same or lower emissions as a 10% aromatics reference fuel in a standardized engine test. Candidate alternative formulations are characterized by five properties: sulfur

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[11] *European Programme on Emissions, Fuels and Engine Technologies, Final Report,* ACEA and Europia.

content, nitrogen content, aromatics content, polycyclic aromatics content, and cetane number. If the formulation passes the emissions test and receives CARB approval, any fuel manufactured under this alternative formulation must not exceed the sulfur, nitrogen, aromatics, and polycyclic aromatics contents of the candidate formulation and must not have a lower cetane number than the candidate formulation.

More than 20 alternative formulations have been approved by CARB. In fact, at this writing (Spring 1998), most of the diesel fuel sold in California is one of these alternative formulation fuels, rather than fuel with a 10% volume maximum aromatics content.

CARB estimates that the use of reformulated diesel fuel has reduced SO_2 emissions by 82%, PM emissions by 25%, and NO_X emissions by 7%, relative to the emissions that would have been generated by the continued use of pre-1993 high sulfur diesel fuel.

FEDERAL DIESEL FUEL EXCISE TAX

The federal government imposes an excise tax on diesel fuel, currently $0.244 per gallon. However, certain fuel uses are tax-exempt or subject to a reduced rate. These uses include: heating; farming; use by state or local governments or nonprofit educational organizations; and boats engaged in fishing or transportation.

Because Congress believed that there was considerable evasion of this tax, the Omnibus Budget Reconciliation Act of 1993 changed some of the diesel tax procedures. Briefly, under the new procedures, the tax is levied on diesel fuel removed from a terminal's truck loading rack unless the fuel is dyed.

Dyed diesel fuel may be used only for nontaxable purposes. Anyone who knowingly sells or uses dyed diesel fuel for taxable purposes or who willfully alters the concentration of dye in diesel fuel is subject to a minimum $10 per gallon penalty. The 1993 Act gives the IRS authority to enforce the diesel fuel tax, including the authority to inspect terminals, dyes, dyeing equipment, and fuel storage facilities; and to stop, detain, and inspect vehicles.

DIESEL FUEL DYEING

A confusing situation for both refiners and purchasers of diesel fuel has arisen because both the IRS and the EPA require the addition of red dye to certain classes of diesel fuel. However, each agency requires that the dye be added to a different class of fuel, at a different concentration, and for a different reason.

- The EPA wants to identify diesel fuel with a high sulfur content in order to ensure that it is not used in on-road vehicles.
- The IRS wants to ensure that tax-exempt low sulfur and high sulfur diesel fuel are not used for taxable purposes.

The EPA Requirements Originally, the EPA's low sulfur diesel regulations required the addition of blue dye to noncomplying high sulfur (>0.05% mass) fuels. But after the Federal Aviation Administration (FAA) expressed concerns that blue-dyed diesel fuel might be confused with the most common aviation gasoline, which already was being dyed blue, the EPA changed the dye from blue to red.

The EPA regulations require "visible evidence of the presence of red dye" to identify high sulfur fuels intended for off-road use. In practice, this requires refiners to add a level of red dye that is equivalent to no more than 0.75 pounds/1000 bbl (ptb) of a solid Solvent Red 26 dye standard. Solvent Red 26 was chosen as the standard because it is a unique chemical available in pure form. Diesel fuels are actually dyed with liquid concentrates of Solvent Red 164 because this dye is more fuel soluble and less costly than the standard. Solvent Red 164 is a mixture of isomers that are very similar to Solvent Red 26, except the former incorporates hydrocarbon *(alkyl)* chains to increase its solubility in petroleum products.

Any red dye observed in the fuel of a vehicle in on-road use triggers a measurement of the fuel's sulfur content. Penalties are assessed based on the actual sulfur content of the fuel, rather than simply on the presence of dye.

The IRS Requirements The IRS regulations require that tax-exempt diesel fuels, both high sulfur and low sulfur, have a minimum level of a Solvent Red 164 dye that is spectrally equivalent to 3.9 ptb of Solvent Red 26 dye standard. This level of dye is more than five times the amount required by the EPA regulations. The IRS contends that the high dye level is necessary to allow detection of tax evasion even after five-fold dilution of dyed fuel with undyed fuel.

4 · Diesel Fuel Refining and Chemistry

Diesel fuel is made from petroleum. All petroleum crude oils are composed primarily of hydrocarbons of the paraffinic, naphthenic, and aromatic classes. Each class contains a very broad range of molecular weights.

As it comes out of the ground, crude oil can be as thin and light-colored as apple cider or as thick and black as melted tar. Thin crude oils have relatively low densities and thus high API gravities.[1] Therefore, they are called *high-gravity* crude oils; conversely, thick crude oils with relatively high densities are *low-gravity* crude oils.

Refining is the process of converting crude oil into high value products. The most important are transportation fuels – gasoline, jet fuel, and diesel fuel. Other important products include liquefied petroleum gas (LPG), heating fuel, lubricating oil, wax, and asphalt. High-gravity crude oils contain more of the lighter products such as gasoline and generally have lower sulfur and nitrogen contents, which makes them easier to refine. However, modern refining processes are capable of turning low-gravity crude oils into high value products. Refining low-gravity crude oils requires more complex and expensive processing equipment, more processing steps, and more energy and, therefore, costs more. The price difference between high-gravity and low-gravity crude oils reflects the refining cost difference.

REFINING PROCESSES

Today's refinery is a complex combination of interdependent processes, the result of a fascinating intertwining of advances in chemistry, engineering, and metallurgy. These processes can be divided into three basic categories:

- **Separation processes** The feed to these processes is separated into two or more components based on some physical property, usually boiling point. These processes do not otherwise change the feedstock. The most common separation process in a refinery is *distillation.*
- **Upgrading processes** These processes improve the quality of a material by using chemical reactions to remove compounds present in trace amounts that give the material the undesired quality. Otherwise the bulk properties of the feedstock are not changed. The most commonly used upgrading process for diesel fuel is *hydrotreating.*
- **Conversion processes** These processes fundamentally change the molecular structure of the feedstock, usually by "cracking" large molecules into small ones, for example *catalytic cracking* and *hydrocracking.*

[1] See *Density and Gravity* sidebar on page 21.

Distillation Distillation is by far the most important and widely used separation process in a petroleum refinery. In large part, petroleum products are defined by their boiling range, and distillation is the process used to separate crude oil or other wide boiling range mixtures into products with narrower boiling ranges.

Crude oil is made up of many thousands of components from light gases that boil below ambient temperature, to very heavy materials that can not be distilled even at temperatures above 1000°F.[2]

In crude petroleum distillation, hot oil is pumped into a distillation column and the lightest hydrocarbons present,[3] usually propane and butane, rise to the top of the column and are removed. Since gasoline is a little heavier, it does not rise quite so high and is drawn off from the side of the column. Kerosene and diesel, the next heavier products, are drawn off at successively lower points on the column. The products that are obtained directly from crude oil distillation are called *straight-run* products, e.g., *straight-run diesel*. The material that is too heavy to vaporize under atmospheric distillation conditions is removed from the bottom of the column *(atmospheric bottoms)*.

The atmospheric bottoms can be fractionated further by a second distillation carried out under reduced pressure. The lower pressure in the distillation column allows some of the heavier components to be vaporized and collected. This process is called *vacuum distillation*, the overhead product is called *vacuum gas oil* (VGO), and the bottoms product is called *vacuum resid*.

Because of the distillation profile of the typical crude, refining by distillation alone has not been able to meet market demand for light fuel products since the early years of this century. It yields too much heavy product and not enough light product. In addition, the quality of light products produced by distillation alone is often poor. The petroleum refiner uses the upgrading and conversion processes to match the barrel to the market.

Upgrading Process Hydroprocessing is a generic term for a range of processes that use hydrogen with an appropriate catalyst[4] to remove undesired components from a refinery stream. The processes run the gamut from mild conditions that remove reactive compounds like olefins and some sulfur and nitrogen compounds *(hydrofinishing)*, to more severe conditions that saturate aromatic rings and remove almost all sulfur and nitrogen compounds *(hydrotreating)*.

Conversion Process Hydrocarbons with higher boiling points (the larger ones left in the distillation bottoms) can be broken down *(cracked)* into lower boiling hydrocarbons by subjecting them to very high temperatures. The discovery of this process *(thermal cracking)* offered a way to correct the mismatch between supply and demand. Thermal cracking began to be used to increase gasoline

DENSITY AND GRAVITY

***Density* (ρ)** **is the mass of a unit volume of material at a selected temperature. For example, the density of water is 0.9990 grams per cubic centimeter (g/cm^3) at 60°F (15.67°C). *Relative density* (RD) – also called *specific gravity* – is the ratio of the density of the material at a selected temperature to the density of a reference material at a selected temperature. For the relative density of petroleum crudes and products in the U.S., the reference material is water and both temperatures are 60°F.**

$$\text{RD } ({}^{60}\!/_{60}{}^\circ\text{F}) = \frac{\rho \text{ sample } (60^\circ\text{F})}{\rho \text{ water } (60^\circ\text{F})}$$

The United States petroleum industry often uses API gravity instead of relative density. The following equation relates API gravity, in degrees API (°API), to relative density.

$$^\circ\text{API} = \frac{141.5}{\text{RD } ({}^{60}\!/_{60}{}^\circ\text{F})} - 131.5$$

While API gravity measurements may be made on liquids at temperatures other than 60°F, the results are always converted to the values at 60°F, the standard temperature.

API gravity is an arbitrary scale developed by the American Petroleum Institute in the early years of the petroleum industry. Density had been used as a primary indicator of quality for liquid products. However the higher value products have lower densities. The API gravity scale was constructed so that API gravity increases inversely to density; therefore, higher value products have higher API gravities. And while the densities of most petroleum products are less than one, the API gravity scale also was constructed so that most values are between 10 and 70.

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[2] In distillation discussions, the terms “light” and “heavy” are used as shorthand for “lower boiling” and “higher boiling.” They do not refer to the density of the materials, although, in general, a lower boiling material also is less dense than a higher boiling material.

[3] Methane and ethane are often present in crude oil as it comes out of the ground. These lightest compounds are removed before the crude oil is transported by pipeline or tanker.

[4] A catalyst is a material that speeds up or otherwise facilitates a chemical reaction without undergoing a permanent chemical change itself.

production starting in 1913. Although by today's standards, the quality and performance of these early cracked products was low, they were sufficient for the engines of the day.

Eventually heat was supplemented by a catalyst, transforming thermal cracking into *catalytic cracking.* Catalytic cracking produces higher quality products than thermal cracking. There are many variations on catalytic cracking, but *fluid catalytic cracking* (FCC) is probably the most widely used conversion process, worldwide. Most of the liquid product from the FCC eventually goes into gasoline; however, one product stream, called *light cycle oil* (LCO), is sometimes blended into diesel fuel.

Hydrocracking is another major conversion process. It is similar to catalytic cracking since it also uses a catalyst, but the reactions take place under a high pressure of hydrogen. The feed to the hydrocracking process is VGO. The large molecules in the VGO are cracked into smaller molecules by breaking carbon-carbon bonds and adding hydrogen atoms in their place. Other chemical changes also occur under hydrocracking conditions: the rings of some aromatic compounds are saturated, and most of the compounds containing sulfur and nitrogen heteroatoms are destroyed. The hydrocracking process yields a large percentage of product in the kerosene and diesel boiling ranges.

THE MODERN REFINERY

A schematic layout of a modern, fully integrated refinery is shown in Figure 4-1 (the diesel fuel related streams are highlighted). Crude oil is fed to the distillation column where straight-run naphtha, kerosene, and diesel are separated at atmospheric pressure.

The bottoms from the atmospheric column are vacuum distilled to obtain VGO for FCC or hydrocracker feed. The VGO may be hydrotreated to reduce sulfur and nitrogen to levels that will improve the performance of the FCC process.

Previously, the vacuum resid might have been used as a low value, high sulfur fuel oil for onshore power generation or marine fuel. But to remain competitive, refiners must wring as much high value product as possible from every barrel of crude. As a result, the vacuum resid may be sent to a resid conversion unit, such as a resid cracker, solvent extraction unit, or coker. These units produce additional transportation fuel or gas oil, leaving an irreducible minimum of resid or coke.

BLENDING

The diesel fuel produced by a refinery is a blend of all the appropriate available streams: straight-run product, FCC light cycle oil, and hydrocracked gas oil. The straight-run diesel may be acceptable as is, or may need minor upgrading. The FCC light cycle oil may need to be hydrotreated to reduce sulfur content.

The refiner must blend the available streams to meet all performance, regulatory, economic, and inventory requirements. Sophisticated computer programs

GAS TO LIQUIDS

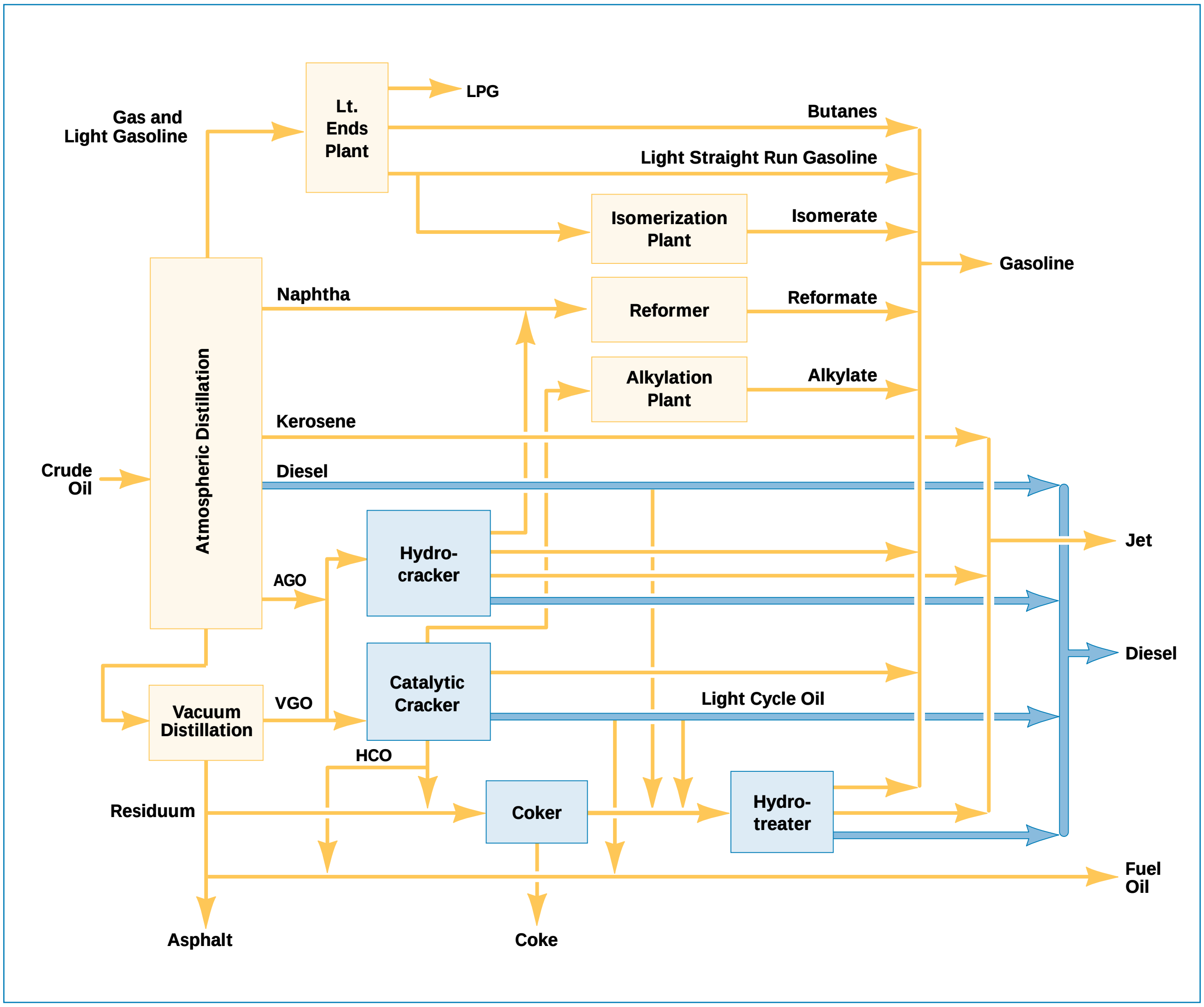
Scientists long have tried to convert natural gas (methane) into liquid fuels. A conversion scheme was worked out in the 1920s by the German chemists Franz Fischer and Hans Tropsch. The *Fischer-Tropsch* process reacts methane with air over a catalyst to create *synthesis gas,* a mixture of carbon monoxide and hydrogen. This gas mixture is then converted to a mixture of liquid hydrocarbons using another catalyst. The diesel boiling range material from this process has a high cetane number and essentially no sulfur or aromatics.

The Fisher-Tropsch process has not seen wide commerical use because it is expensive. It is receiving new interest lately because of its potential to bring "remote" natural gas to traditional markets. Researchers claim that recent advances make the process economically competitive, and as a result, several major projects are being planned. If the projects are successful, they will provide a new source of high quality diesel fuel.

BIODESULFURIZATION

Biodesulfurization utilizes specific bacteria to metabolize some of the sulfur compounds found in crude oil. The process brings the oil together with an aqueous suspension of the bacteria and lets the bugs eat to their hearts' content. The process takes place at near ambient conditions and, so it is less energy intensive than hydrotreating or other desulfurization processes. Demonstration projects for diesel biodesulfurization are under way. If the process proves to be technically and economically feasible, refiners will have a new upgrading process at their command. (Refiners have used bacteria for years to remove hydrocarbons from wastewater.)

Figure 4-1
The Modern Refinery



have been developed to optimize all aspects of refinery operation, including the final blending step. Refineries are optimized for overall performance, not just for the production of diesel fuel.

The refiner really has only limited control over the detailed composition of the final diesel blend. It is determined primarily by the composition of the crude oil feed, which is usually selected based on considerations of availability and cost. While the chemical reactions that occur in the conversion processes involve compositional changes, they are not specific enough to allow for much tailoring of the products. Yet, despite these limitations, refineries daily turn out large volumes of on-test products. Truly a remarkable achievement!

ABOUT HYDROCARBONS

Hydrocarbons are organic compounds composed entirely of carbon and hydrogen atoms. There are four major classes of hydrocarbons: paraffins, naphthenes, olefins, and aromatics. Each class is a family of individual hydrocarbon molecules that share a common structural feature, but differ in size (number of carbon atoms) or geometry. The classes also differ in the ratio of hydrogen to carbon atoms and in the way the carbon atoms are bonded to each other.

Paraffins Paraffins have the general formula C_nH_{2n+2}, where “n” is the number of carbon atoms *(carbon number)* in the molecule. There are two subclasses of paraffins: *normal paraffins* and *isoparaffins.*

Normal paraffins have carbon atoms linked to form chain-like molecules, with each carbon – except those at the ends – bonded to two others, one on either side. Isoparaffins have a similar carbon backbone, but they also have one or more carbons branching off from the backbone. Normal decane and 2,4-dimethyloctane have the same chemical formula, $C_{10}H_{22}$, but different chemical and physical properties. Compounds like this, with the same chemical formula but a different arrangement of atoms, are called *structural isomers.*

Naphthenes Naphthenes have some of their carbon atoms arranged in a ring. The naphthenes in diesel fuel have rings of five or six carbons. Sometimes two or more rings are fused together, with some carbons shared by adjacent rings. Naphthenes with one ring have the general formula C_nH_{2n}.

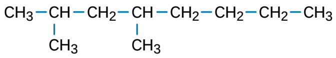
Olefins Olefins are similar to paraffins but have fewer hydrogens and contain at least one double bond between a pair of carbon atoms. Olefins rarely occur in crude oil; they are formed by certain refinery processes. Like paraffins, olefins with four or more carbons can exist as structural isomers. Olefins with one double bond have the general formula C_nH_{2n}, the same as naphthenes.

n-Paraffin

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

n-Decane $C_{10}H_{22}$

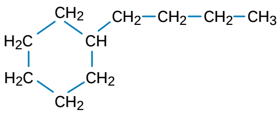
Isoparaffin



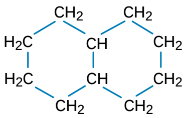
$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_2-CH_3$

2, 4-Dimethyloctane $C_{10}H_{22}$

Naphthenes



Butylcyclohexane $C_{10}H_{20}$



Decalin $C_{10}H_{18}$

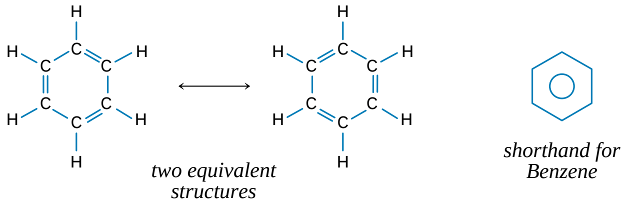
Olefin

$CH_2=CH-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

1-Decene $C_{10}H_{20}$

Aromatics As with naphthenes, some of the carbon atoms in aromatics are arranged in a ring, but they are joined by aromatic bonds, not the single bonds found in naphthenes. Aromatic hydrocarbon rings contain six carbon atoms. Benzene is the simplest aromatic compound. The benzene structure was originally conceptualized as two equivalent structures with alternating single and double bonds. Each structure continually transformed itself into the other as the double bonds flipped back and forth between different pairs of carbon atoms. Now, we know that all the carbon to carbon bonds in benzene are equivalent. The shorthand representation of benzene is a hexagon with a circle inside representing the aromatic bonds. One-ring aromatics have the general formula C_nH_{2n-6}. *Polycyclic aromatics* are compounds with two or more aromatic rings. These rings are often fused together, with some carbons being shared by adjacent rings.

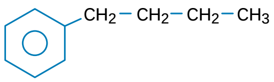
Aromatic Compounds



two equivalent structures

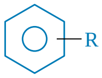
shorthand for Benzene

Benzene C_6H_6



Butylbenzene $C_{10}H_{14}$

2-Methylnaphthalene $C_{11}H_{10}$
Polycyclic aromatic or polynuclear aromatic



Substituted Aromatic:

R *represents an alkyl (hydrocarbon) group that can be bonded to any one of the carbons in the benzene ring.*

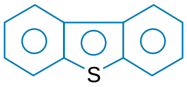
Paraffins and naphthenes are classified as *saturated hydrocarbons* because no more hydrogen can be added to them without breaking the carbon backbone. Aromatics and olefins are classified as *unsaturated hydrocarbons.* They contain carbon to carbon double bonds or aromatic bonds that can be converted to single bonds by adding hydrogen atoms to the adjacent carbons. When straight-chain olefins are saturated with hydrogen, they become paraffins. When aromatics are completely saturated with hydrogen, they become naphthenes; when they are partially saturated, they become cyclic olefins.

Some molecules contain structural features characteristic of two or more hydrocarbon classes. For example, a molecule could contain an aromatic ring, a naphthenic ring, and a paraffinic chain. How should this molecule be classified? Chemists have established a hierarchy of hydrocarbon structural features, with aromatics at the top, followed by olefins, naphthenes, and paraffins. A compound with features of more than one class is placed in the class highest in the hierarchy. So, in our example, the molecule is classified as an aromatic.

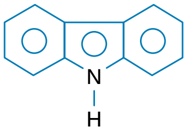
OTHER COMPOUNDS

While carbon and hydrogen are the predominant elements in crude oil, small amounts of sulfur, nitrogen, and oxygen are also present. These elements are called *heteroatoms* ("other" atoms). When heteroatoms are bound into molecular structures with carbon and hydrogen, the resulting compounds no longer are hydrocarbons. Typical examples of non-hydrocarbon compounds found in diesel include dibenzothiophene and carbazole. Although these compounds are present in small amounts, they play a large role in determining certain fuel properties.

Heteroatomic Compounds



Dibenzothiophene

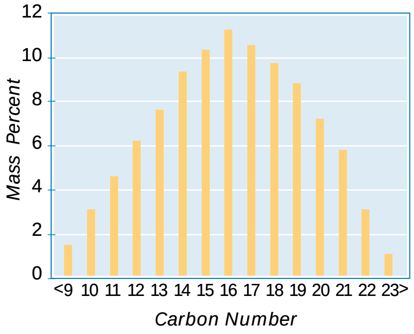


Carbazole

DIESEL FUEL CHEMISTRY

Figure 4-2 illustrates a typical carbon number distribution for No. 2-D diesel fuel, and Figure 4-3 shows a typical distillation profile. Diesel fuel is a very complex mixture of thousands of individual compounds, most with carbon numbers between 10 and 22. Most of these compounds are members of the paraffinic, naphthenic, or aromatic class of hydrocarbons. These three classes of hydrocarbons have different chemical and physical properties. Different relative proportions of the three classes is one of the factors that make one diesel fuel different from another. We will show how the properties of the three classes influence the properties of the whole fuel and affect its performance in a diesel engine.

Figure 4-2
Typical Carbon Number Distribution – No. 2 Diesel Fuel



Hydrocarbon Properties

Figure 4-4 lists the boiling points and freezing points of typical diesel fuel hydrocarbons.

Boiling Point For compounds in the same class, boiling point increases with carbon number. For compounds of the same carbon number, the order of increasing boiling point by class is isoparaffin, n-paraffin, naphthene, and aromatic. The boiling point difference (100°–150°F or 60°–80°C) between isoparaffins and aromatics of the same carbon number is larger than the boiling point difference (about 35°F or 20°C) between compounds of the same class that differ by one carbon number. Thus, the compounds that boil at about 500°F, the middle of the diesel fuel boiling range, might be C_{12} aromatics, C_{13} naphthenes, C_{14} n-paraffin, and C_{15} isoparaffins.

Figure 4-3
Typical Distillation Profile – No. 2 Diesel Fuel

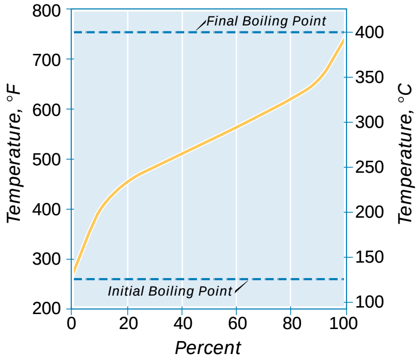


Figure 4-4
Boiling Point and Freezing Point of Representative Diesel Fuel Hydrocarbons

Compound	Chemical Formula	Hydrocarbon Class	Boiling Point, °F	Freezing Point, °F
Naphthalene	$C_{10}H_{8}$	Aromatic	424	176
Tetralin	$C_{10}H_{12}$	Aromatic	406	-31
cis-Decalin	$C_{10}H_{18}$	Naphthene	385	-45
1, 3-Diethylbenzene	$C_{10}H_{14}$	Aromatic	358	-119
n-Butylcyclohexane	$C_{10}H_{20}$	Naphthene	358	-103
n-Pentylcyclopentane	$C_{10}H_{20}$	Naphthene	358	-117
Decane	$C_{10}H_{22}$	n-Paraffin	345	-22
Anthracene	$C_{14}H_{10}$	Aromatic	646	419
1-Pentylnaphthalene	$C_{15}H_{18}$	Aromatic	583	-11
n-Nonylcyclohexane	$C_{15}H_{30}$	Naphthene	540	14
n-Decylcyclopentane	$C_{15}H_{30}$	Naphthene	534	-8
n-Pentadecane	$C_{15}H_{32}$	n-Paraffin	520	50
2-Methyltetradecane	$C_{15}H_{32}$	Isoparaffin	509	18
1-Decylnaphthalene	$C_{20}H_{28}$	Aromatic	714	59
n-Tetradecylbenzene	$C_{20}H_{34}$	Aromatic	669	61
n-Tetradecylcyclohexane	$C_{20}H_{40}$	Naphthene	669	77
n-Pentadecylcyclopentane	$C_{20}H_{40}$	Naphthene	667	63
Eicosane	$C_{20}H_{42}$	n-Paraffin	651	97
2-Methylnonadecane	$C_{20}H_{42}$	Isoparaffin	642	64

Freezing Point Freezing points (melting points) also increase with molecular weight, but they are strongly influenced by molecular shape. Molecules that fit more easily into a crystal structure have higher freezing points than other molecules. This explains the high melting points of n-paraffins and unsubstituted aromatics, compared to the melting points of isoparaffins and naphthenes of the same carbon number.

Density Figure 4-5 lists density and heat of combustion (heating value) for some representative diesel fuel hydrocarbons. For compounds of the same class, density increases with carbon number. For compounds with the same carbon number, the order of increasing density is paraffin, naphthene, and aromatic.

Figure 4-5

Density and Heat of Combustion for Representative Diesel Fuel Hydrocarbons

Compound	Hydrocarbon Class	Carbon Number	Density, 20°C, g/cm^3	Net Heat of Combustion, 25°C, Btu/Lb	Net Heat of Combustion, 25°C, Btu/Gal
Naphthalene	Aromatic	10	1.175	16,704	163,800
Tetralin	Aromatic	10	0.9695	17,422	140,960
1,3-Diethylbenzene	Aromatic	10	0.8639	17,792	128,270
n-Butylcyclohexane	Naphthene	10	0.7992	18,666	124,500
n-Pentylcyclopentane	Naphthene	10	0.7912	18,738	123,720
Decane	n-Paraffin	10	0.7301	19,018	115,880
2,2-Dimethyloctane	Isoparaffin	10	0.7245	18,979	114,750
Anthracene	Aromatic	14	1.251	16,514	172,410
n-Nonylbenzene	Aromatic	15	0.8558	18,120	129,410
n-Nonylcyclohexane	Naphthene	15	0.816	18,672	127,150
n-Decylcyclopentane	Naphthene	15	0.811	18,721	126,710
n-Pentadecane	n-Paraffin	15	0.7684	18,908	121,250
n-Tetradecylbenzene	Aromatic	20	0.8549	18,264	130,310
n-Tetradecylcyclohexane	Naphthene	20	0.825	18,678	128,590
n-Pentadecylcyclopentane	Naphthene	20	0.8213	18,712	128,260
Eicosane	n-Paraffin	20	0.7843	18,853	123,400

Heating Value For compounds with the same carbon number, the order of increasing heating value by class is aromatic, naphthene, and paraffin on a weight basis. However, the order is reversed for a comparison on a volume basis, with aromatic highest and paraffin lowest.

This same trend holds with fuels *(see Figure 4-6)*. Lighter (less dense) fuels, like gasoline, have higher heating values on a weight basis; whereas the heavier (more dense) fuels, like diesel, have higher heating values on a volume basis.

Cetane Number Cetane number also varies systematically with hydrocarbon structure *(see Figure 4-7)*. Normal paraffins have high cetane numbers that increase with molecular weight. Isoparaffins have a wide range of cetane numbers, from about 10 to 80. Molecules with many short side chains have low cetane numbers; whereas those with one side chain of four or more carbons have high cetane numbers.

Figure 4-6

Typical Density and Net Heating Value of Different Fuels

Fuel	Density, g/cm^3	Net Heating Value, Btu/lb.	Net Heating Value, Btu/gal.
Regular gasoline	0.735	18,630	114,200
Premium gasoline	0.755	18,440	116,200
Jet fuel	0.795	18,420	122,200
Diesel fuel	0.850	18,330	130,000

THERMAL EXPANSION

Like all liquids, diesel fuel slightly expands in volume as its temperature increases. The *coefficient of thermal expansion* measures the rate of the expansion. A typical value of the coefficient of thermal expansion for diesel fuel is 0.00046 per degree Fahrenheit. Using this value, 1.000 gallon of diesel fuel at 20°F will expand to 1.037 gallons at 100°F.

Naphthenes generally have cetane numbers from 40 to 70. Higher molecular weight molecules with one long side chain have high cetane numbers; lower molecular weight molecules with short side chains have low cetane numbers.

Aromatics have cetane numbers ranging from zero to 60. A molecule with a single aromatic ring with a long side chain will be in the upper part of this range; a molecule with a single ring with several short side chains will be in the lower part. Molecules with two or three aromatic rings fused together have cetane numbers below 20.

Viscosity Viscosity is primarily related to molecular weight and not so much to hydrocarbon class. For a given carbon number, naphthenes generally have slightly higher viscosities than paraffins or aromatics.

Figure 4-7

Cetane Number of Representative Diesel Fuel Hydrocarbons

Compound	Hydrocarbon Class	Chemical Formula	Cetane Number
n-Decane	n-Paraffin	$C_{10}H_{22}$	76
n-Pentadecane	n-Paraffin	$C_{15}H_{32}$	95
n-Hexadecane*	n-Paraffin	$C_{16}H_{34}$	100
n-Eicosane	n-Paraffin	$C_{20}H_{42}$	110
3-Ethyldecane	Isoparaffin	$C_{12}H_{26}$	48
4,5-Diethyloctane	Isoparaffin	$C_{12}H_{26}$	20
Heptamethylnonane*	Isoparaffin	$C_{16}H_{34}$	15
8-Propylpentadecane	Isoparaffin	$C_{18}H_{38}$	48
7,8-Diethyltetradecane	Isoparaffin	$C_{18}H_{38}$	67
9,10-Dimethyloctane	Isoparaffin	$C_{20}H_{42}$	59
Decalin	Naphthene	$C_{10}H_{18}$	48
3-Cyclohexylhexane	Naphthene	$C_{12}H_{24}$	36
2-Methyl-3-cyclohexylnonane	Naphthene	$C_{16}H_{32}$	70
2-Cyclohexyltetradecane	Naphthene	$C_{20}H_{40}$	57
1-Methylnaphthalene*	Aromatic	$C_{11}H_{10}$	0
n-Pentylbenzene	Aromatic	$C_{11}H_{16}$	8
Biphenyl	Aromatic	$C_{12}H_{10}$	21
1-Butylnaphthalene	Aromatic	$C_{14}H_{16}$	6
n-Nonylbenzene	Aromatic	$C_{15}H_{24}$	50
2-Octylnaphthalene	Aromatic	$C_{18}H_{24}$	18
n-Tetradecylbenzene	Aromatic	$C_{20}H_{34}$	72

* Primary reference material for cetane number scale

Figure 4-8 summarizes the relationships between hydrocarbon class and fuel properties. Normal paraffins have excellent cetane numbers, but very poor cold flow properties and low volumetric heating values. Aromatics have very good cold flow properties and volumetric heating values, but very low cetane numbers. Isoparaffins and naphthenes are intermediate, with values of these properties between those of normal paraffins and aromatics.

Figure 4-8

Relationship of Hydrocarbon Class Properties to Fuel Properties

Fuel Property	Normal Paraffin	Isoparaffin	Naphthene	Aromatic
Cetane number	++	0/+	0/+	0/–
Low temperature operability	–	0/+	+	+
Volumetric heating value	–	–	0	+

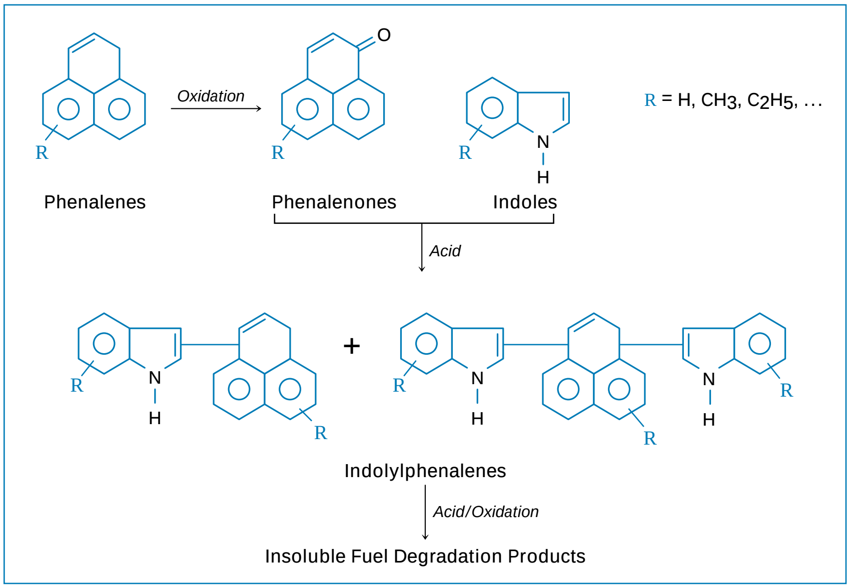
+ Indicates a positive or beneficial effect on the fuel property.
0 Indicates a neutral or minor effect.
– Indicates a negative or detrimental effect.

CHEMISTRY OF DIESEL FUEL INSTABILITY

For the most part, instability involves the chemical conversion of precursors to species of higher molecular weight with limited fuel solubility. The precursors are certain nitrogen and/or sulfur containing compounds, organic acids, and reactive olefins. The conversion process often involves oxidation of the precursors. Certain dissolved metals, especially copper, contribute by functioning as oxidation catalysts. Fuel solvency also plays a role, because the development of insolubles is always a function of both the presence of higher molecular weight species and the capacity of the fuel to dissolve them.

Figure 4-9

Sequence of Reactions Leading to Formation of Insolubles in Diesel Fuel[5]



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[5] Adapted from Pedley et al. *"Storage Stability of Petroleum-derived Diesel Fuel," Fuel* **68**, pp. 27–31 (1989).

One well-established mechanism by which insolubles are formed is the acid-catalyzed conversion of phenalenones and indoles to complex indolylphenalene salts *(see Figure 4-9)*. Phenalenones are formed by oxidation of certain reactive olefins; indoles occur naturally in certain blend components of diesel fuel. The required organic acid is either present in a blend component or is generated by the oxidation of mercaptans to sulfonic acids. This mechanism can be interrupted by various means, e.g., by omitting acidic species and/or its precursors from the fuel blend, by destroying the necessary precursors by hydrotreating, or by adding antioxidant or basic stabilizer additives.

Contrary to intuition, two fuels that, by themselves, each have good stability may form a less stable blend when they are combined. In this case, each fuel contains some of the precursors needed for the formation of higher molecular weight species. Only when the fuels are mixed are all the precursors available, enabling the conversion to proceed.

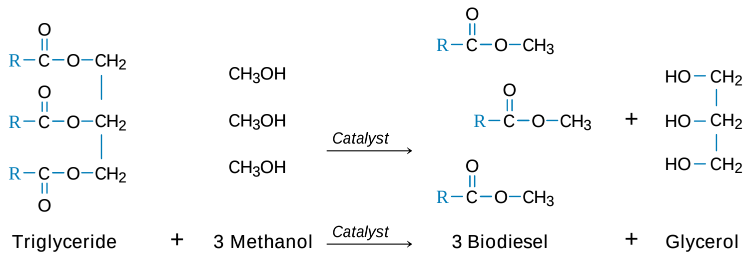
Another example of an unexpected interaction involves 2-ethylhexyl nitrate (EHN) (diesel ignition improver or cetane number improver). The addition of EHN to a fuel or the blending of fuels, one of which contains EHN, may increase thermal instability because the decomposition of EHN promotes the reactions that lead to higher molecular weight species.

BIODIESEL

Biodiesel has been in the news in recent years as a possible alternative to conventional, petroleum derived diesel. The main reason for the interest is that biodiesel is a renewable source of energy. In general usage, the term *biodiesel* covers a variety of materials made from vegetable oils or animal fats. In the United States, soybean oil is the largest source of biodiesel, although oil from other plants can be used as well.

Biodiesel is a mixture of fatty acid methyl esters. Vegetable oils, which chemically are triglycerides of fatty acids, are not good biodiesels. However, the oils can be combined with methanol in a process known as *transesterification* to produce a material with better properties *(see Figure 4-10)*.

Figure 4-10
Transesterification of Vegetable Oil to Biodiesel



R *is typically 16 or 18 carbons and may contain one to three carbon-carbon double bonds.*

The resulting mixture of fatty acid methyl esters has chemical and physical properties similar to those of conventional diesel fuel. Figure 4-11 compares some typical properties of soybean-derived biodiesel (sometimes called *methyl soyate* or *SoyDiesel*) to those of low sulfur diesel fuel.

Figure 4-11

Comparison of Typical Properties of Biodiesel and Low Sulfur Diesel

Fuel Property	Biodiesel (typical)	Low Sulfur (typical)	ASTM D 975 Specification
Flash point, °C	100	60	52 min.
Viscosity, 40°C, cSt	4.7	3.2	1.9–4.1
Sulfur, % mass	<0.01	0.03	0.05 max.
Cetane number	48–52	45	40 min.
Heating value, net, Btu/gallon	128,000	130,000	
Relative density, 15°C	0.88	0.83–0.86	

Source: National Soy Diesel Development Board.

While diesel engines can run on neat (100%) biodiesel, most of the testing in this country has been done on blends of biodiesel and low sulfur diesel. A blend of 20% biodiesel with 80% low sulfur diesel (sometimes called B20 or BD-20) has been tested in city bus fleets across the country.

Limited testing has shown that this fuel produces lower emissions of particulate matter, hydrocarbons, and carbon monoxide than conventional diesel fuel; however, the same emission reduction can also be achieved by installing a catalytic converter in the vehicle exhaust system. Emissions of NO_X can be slightly higher than with conventional diesel, unless the fuel system injection timing is optimized for the fuel.

The energy content of neat biodiesel is slightly lower than that of conventional diesel, but limited road testing has shown no appreciable loss in performance or mileage. Neat biodiesel has good lubricity properties and contains essentially no sulfur or aromatics. However, it has a relatively high pour point, which could limit its use in cold weather. Biodiesel is biodegradable, but this property may lead to increased biological growth during storage. Biodiesel is also more susceptible to oxidative degradation than petroleum diesel.

The main disadvantage of biodiesel is its cost, which, as of this writing is two-thirds higher than that of conventional diesel fuel. Until the price comes down, its use will probably be limited to situations where it is subsidized or where the potential environmental benefits offset the additional cost. For example, biodiesel is more widely used in Europe where environmental regulations and tax subsidies make it practical.

5 · Diesel Fuel Specifications and Testing

It has been critical to the successful development of diesel fuel and diesel-powered vehicles to have consensus among refiners, vehicle and engine manufacturers, and other interested parties on the characteristics of diesel fuel necessary for satisfactory performance and reliable operation. In the United States, this consensus is reached under the auspices of the American Society for Testing and Materials (ASTM).

ASTM is an organization of committees. Committee D-2 *(Petroleum Products and Lubricants)* is responsible for diesel fuel specifications and test methods. The committee members bring to the D-2 forum the viewpoints of the large number of groups who are interested in and/or are affected by diesel fuel specifications. These groups include:

- Individual refiners
- Petroleum marketing organizations
- Additive suppliers
- Vehicle and engine manufacturers
- Governmental regulatory agencies, like the Environmental Protection Agency and state regulatory agencies
- General interest groups, consumer groups, and consultants

Committee D-2 also turns to groups like the Society of Automotive Engineers (SAE) and the Coordinating Research Council (CRC) when they need reliable technical data to help establish a specification or develop a test method.

Figure 5-1 lists the diesel fuel properties that have been identified as important and indicates how they affect performance. The figure also notes whether the property is determined by the bulk composition of the fuel or by the presence or absence of minor components. And it notes the time frame of the performance effect – whether the effect typically occurs immediately or after hundreds of hours of operation *(long-term)*.

SPECIFICATIONS

Not surprisingly, most of the properties in Figure 5-1 are addressed by ASTM D 975 – *Standard Specification for Diesel Fuel Oils.* D 975 sets limits *(requirements)* for the values of these properties. These requirements are listed in Figure 5-2 for the five grades of diesel fuel defined by the specification. D 975 also indicates the standard test methods that are to be used to measure the values of the properties. These methods are described in the *Test Methods* section at the end of this chapter.

Most of the requirements of D 975 are the minimum ones needed to guarantee acceptable performance for the majority of users. In addition, the specification recognizes some requirements established by the EPA to reduce emissions. For a variety of reasons, other organizations may establish additional requirements:

- **State governments** To reduce emissions, CARB established additional requirements for vehicular diesel fuel which became effective in 1993.
- **Pipelines** Some companies that transport diesel fuel have limits for density and pour point, properties that D 975 does not limit.
- **Some purchasers** The U.S. Department of Defense (DOD) formerly purchased fuels meeting military specifications that often included special requirements in addition to the D 975 requirements. Now the DOD buys commercial fuel when possible.

Figure 5-1

Relationship of Diesel Fuel Properties to Composition and Performance

Property	Property Type*	Effect of Property on Performance	Time Frame of Effect
Flash point	Minor	Safety in handling and use – not directly related to engine performance	—
Water and sediment	Minor	Affects fuel filters and injectors	Long-term
Volatility	Bulk	Affects ease of starting and smoke	Immediate
Viscosity	Bulk	Affects fuel spray atomization and fuel system lubrication	Immediate and Long-term
Ash	Minor	Can damage fuel injection system and cause combustion chamber deposits	Long-term
Sulfur	Minor	Affects particulate emissions, cylinder wear, and deposits	Particulates: Immediate Wear: Long-term
Copper strip corrosion	Minor	Indicates potential for corrosive attack on metal parts	Long-term
Cetane number	Bulk	Measure of ignition quality – affects cold starting, combustion and emissions	Immediate
Cloud point and pour point	Minor	Affects low temperature operability	Immediate
Carbon residue	Minor	Measures coking tendency of fuel, may relate to engine deposits	Long-term
Heating value (energy content)	Bulk	Affects fuel economy	Immediate
Density	Bulk	Affects heating value	Immediate
Stability	Minor	Indicates potential to form insolubles during use and/or in storage	Long-term
Lubricity	Minor	Affects fuel pump and injector wear	Long-term (typically)
Water separability	Minor	Affects ability to produce dry fuel	—

* A *bulk* property is one that is determined by the composition of the fuel as a whole. A *minor* property is one that is determined by the presence or absence of small amounts of particular compounds.

Figure 5-2

ASTM D 975 Requirements for Diesel Fuel Oils

Property	Test Method*	Low Sulfur No. 1-D	No. 1-D	Low Sulfur No. 2-D	No. 2-D	No. 4-D
Flash point, °C, min	D 93	38	38	52	52	55
Water and sediment, % vol, max	D 2709	0.05	0.05	0.05	0.05	
	D 1796					0.50
Distillation temperature, °C, 90% vol recovered	D 86					
min				282	282	
max		288	288	338	338	
Kinematic viscosity, 40°C, cSt	D 445					
min		1.3	1.3	1.9	1.9	5.5
max		2.4	2.4	4.1	4.1	24.0
Ash, % mass, max	D 482	0.01	0.01	0.01	0.01	0.1
Sulfur, % mass, max	D 2622	0.05	0.50	0.05	0.50	2.00
Copper strip corrosion, 3 hr at 50°C, max rating	D 130	No. 3	No. 3	No. 3	No. 3	
Cetane number, min	D 613	40	40	40	40	30
One of the following:						
1) Cetane index, min	D 976	40		40		
2) Aromaticity, % vol, max	D 1319	35		35		
Ramsbottom carbon residue on 10% distillation residue, % mass, max	D 524	0.15	0.15	0.35	0.35	

* All "Dxx" methods are ASTM standards.

A refiner must ensure that its fuel meets all the relevant requirements, not just those of D 975.

Diesel fuel specifications in other countries are similar, but not identical, to those in the U.S. Figure 5-3 compares the D 975 specification for low sulfur No. 2-D to European and Japanese specifications for comparable grades.

Figure 5-3

Comparison of U.S., European, and Japanese Specifications for a Comparable Grade of Diesel Fuel

Property	US: ASTM D 975, Low Sulfur No. 2-D	Europe: CEN 590: Grades A-F	Japan: JIS K 2204, Grade No. 2
Density			
15°C, g/cm^3		0.820–0.860	
Kinematic viscosity			
38°C, cSt			2.0 min
40°C, cSt	1.9–4.1	2.0–4.5	
Sulfur, % mass, max	0.05	0.05	0.05
Cetane number, min	40	49	45
Distillation temperature, °C % vol recovered			
65		250 min	
85		350 max	
90	282–338		330–350
95		370 max	

PREMIUM DIESEL

In recent years, environmental regulations have had a significant effect on the formulation of diesel fuel. The introduction of new fuels, coupled with the rapid changes in engine design to meet new emission regulations, has created the need to address several fuel properties to ensure proper performance, while also minimizing engine maintenance problems.

Some fuel users believe that in some special operations related to some equipment or in a certain geographic location, they can benefit from a fuel supply with properties beyond the minimum ASTM D 975 specifications. A number of fuel suppliers market such "designer" fuels and charge a higher price. The fuel with these enhancements is often called *premium diesel*, although other names are also used. So far, two groups have proposed definitions for premium diesel. These groups are the National Conference on Weights and Measures (NCWM) and the Engine Manufacturers Association (EMA).

The premium diesel concept is not the same as that of the premium gasoline. Gasoline engines of certain types and compression ratios require a higher octane fuel to avoid knocking. Therefore, premium gasoline is required for these vehicles and is provided by all fuel suppliers. Premium diesel, on the other hand, is related to varying one or more fuel properties. Some of the more-talked-about fuel properties are: cetane number, low temperature operability, stability, lubricity, detergency, and heating value. The suppliers of premium diesel fuel evaluate their marketing area and provide a fuel that has one or more of these improved properties. The level of improvement in each property varies from one supplier to another.

National Conference on Weights and Measures The NCWM addressed the premium diesel issue to ensure that the consumer receives a functional benefit for the higher price. The NCWM organized a task force of representatives from the oil industry, additive manufacturers, independent labs, and government agencies to define premium diesel. The task force was guided by two principles: functionality and practicality. A premium fuel property must be one that, when enhanced from its average value in conventional diesel, provides a *functional* benefit to consumers – a benefit that has been technically demonstrated. And there must be a *practical* means of enforcing the enhanced value – it must be measurable by a recognized test method accepted by the industry. For example, the task force considered lubricity as a possible premium fuel property. There was general agreement that lubricity is important and that an enhanced value, in some cases, would provide a functional benefit. However, a lubricity requirement for premium diesel was put on hold because the available test methods have poor precision and do not accurately predict performance for all fuel/additive combinations.

In late 1997, the NCWM task force recommended that a fuel must meet any two of the five criteria listed in Figure 5-4 to merit the "premium" label.

The NCWM will vote on the proposed regulation in July 1998. If approved, the definition becomes a model law. As such, it automatically will be adopted by some states; elsewhere, it will only become effective if a state specifically adopts it.

Figure 5-4

Fuels Must Meet Two of Five Properties to Meet the NCWM Premium Diesel Definition

Fuel Property	Test Method*	NCWM Premium Diesel Recommendation
Heating value, gross, Btu/gallon, min	D 240	138,700
Cetane number, min	D 613	47.0
Low temperature operability	D 2500 or D 4539	2°C maximum above the D 975 tenth percentile minimum ambient air temperature
Thermal stability, 180 minutes, 150°C, reflectance, min	Octel F21-61	80%
Fuel injector cleanliness	L-10 Injector	
Flow loss, % max		6.0
CRC rating, % max		10.0

* All "Dxx" methods are ASTM standards.

Engine Manufacturers Association The EMA has issued a Recommended Guideline (FQP-1A) for a premium diesel fuel. The recommended values, the ASTM specifications for Low Sulfur No. 2-D, and the 1996 U.S. average for on-road diesel are listed in Figure 5.5.

Here is some of the guideline's explanatory text:

This Recommended Guideline of the Engine Manufacturers Association is intended to define a diesel fuel that is superior in quality to the commercial fuel specification ASTM D 975.

The diesel fuel is considered to be "premium" insofar as it may assist in improving the performance and durability of engines currently in use and those to be produced prior to 2004. It is not intended to enable diesel engines to meet 1998 federal emission standards or, in general, to improve engine exhaust emissions.

The most significant aspects of this Recommended Guideline are its requirements for a minimum fuel lubricity, increased cetane number and improved cold weather performance. These properties, … should help address many current customer satisfaction and engine performance issues.

Figure 5-5

EMA FQP-1A Guideline, ASTM D 975 Specification, and 1996 U.S. Average Properties for Low Sulfur No. 2-D Diesel Fuel

Property	Test Method*	EMA FQP-1A	ASTM D 975	1996 U.S. Average(1)
Flash point, °C, min	D 93	52	52	73
Water and sediment, % vol, max	D 2709		0.05	
Water, ppm max	D 1744	200		
Sediment, ppm max	D 2276 or D 5452	10		
Distillation, °C, % vol recovery	D 86			
90% max		332	338	324, 320(2)
95% max		355		
Viscosity, 40°C, cSt	D 445	1.9–4.1	1.9–4.1	2.58
Ash, % mass, max	D 482	0.01	0.01	0.002
Sulfur, % mass, max	D 2622	0.05	0.05	0.033
Copper corrosion, max	D 130	3b	3b	
Cetane number, min	D 613	50	40	48, 45(2)
Cetane index, min	D 4737	45	40	48
Ramsbottom carbon on 10% residue, % mass, max	D 524	0.15	0.35	0.067
API gravity, max	D 287	39		35.6, 34.3(2)
Lubricity, g, min	D 6078(3)	3100		
Accelerated stability, mg/L, max	D 2274	15		
Detergency	L10 Injector			
CRC rating, max		10.0		
Depositing test, % flow loss, max		6.0		
Low temperature flow, °C	D 2500 or D 4539	(4)		
Cloud point, °C			appropriate to climate	

* All "Dxx" methods are ASTM standards.

(1) C.L. Dickson and G.P. Sturm, Jr., *Diesel Fuel Oils*, 1996, NIPER-197 PPS 96/5.

(2) *American Petroleum Institute/National Petroleum Refiners Association Survey of Refining Operations and Product Quality. Final Report* July 1997.

(3) Alternatively, lubricity can be measured by D 6079 with a maximum wear scar diameter of 0.45 μ at 60°C.

(4) Diesel fuels must pass the *Cloud Point* (D 2500) or *Low Temperature Flow Test* (D 4539) at the use temperature.

CURRENT ASTM D 975 ISSUES

ASTM specifications are living documents; they are continually being reviewed and updated as new performance information is acquired, as use requirements change, or as new analytical techniques are developed. Diesel fuel properties currently under review by the specification committee include cetane number, cetane index, low temperature operability, stability, lubricity, and detergency.

Some of these properties, such as cetane number and cetane index, are already included in the D 975 requirements, while the others are not. These other properties are not being ignored; most informed parties acknowledge that they affect performance or maintenance. But adding a new property to an ASTM specification is a time consuming process; it requires developing and/or validating a test method, developing technical data to support the new requirement and, finally, reaching consensus. In our view, there are at least two barriers to adding specifications for properties such as stability, lubricity, and detergency to D 975:

- The lack of standardized test methods applicable to all fuel compositions and fuel/additive combinations
- The large gray areas between clearly acceptable and clearly unacceptable values

Because much of the "grayness" is the result of engine-to-engine and vehicle-to-vehicle variation, it is difficult and costly to define the relationship between fuel property and performance in this intermediate region. In spite of the problems, the industry continues to explore these properties with the goal of reaching consensus on test methods and requirements.

To illustrate the considerations that go into changing or adding a property, the following paragraphs discuss current issues concerning cetane index, low temperature operability, and lubricity.

Cetane Index The two cetane index methods most commonly used to estimate cetane number, ASTM D 976 and ASTM D 4737 *(see page 41)*, were developed in 1966 and 1987, respectively. These methods are based on correlations between physical properties of diesel fuels and their cetane numbers. However, diesel fuels have changed since these correlations were developed. In 1993 two new diesel fuels were introduced: EPA low sulfur diesel for on-road use in the U.S., and CARB low aromatics diesel for use in California. Since these types of diesel fuels were not in use when the cetane index methods were developed, it isn't surprising that the correlations between physical properties and cetane number does not work as well for the new fuels. ASTM is working to develop a new correlation that accurately predicts the cetane numbers of today's fuels.

Low Temperature Operability It is the combination of fuel behavior and fuel system design that causes filter plugging, not either one alone. While some fuel systems plug at the cloud point temperature, many others can operate several degrees below the cloud point. This is because low temperature filterability depends on the size and shape of wax crystals, not merely on their presence. There has been considerable effort to develop a laboratory test that correlates with field performance, especially for additized fuels. It has been focused on dynamic tests that simulate flow through a filter in the fuel system, rather than on static physical property tests, like cloud point.

One dynamic test that has been widely accepted in Europe is the *Cold Filter Plugging Point of Distillate Fuels* (CFPP).[1] In this test, the sample is cooled by immersion in a constant temperature bath. Thus the cooling rate is non-linear, but fairly rapid – about 40°C/hour. The CFPP is the temperature of the sample when 20 ml of the fuel first fails to pass through a wire mesh in less than 60 seconds. CFPP appears to over estimate the benefit obtained from the use of certain additives, especially for North American vehicles.

A similar dynamic test was developed in the U.S.: the *Low-Temperature Flow Test* (LTFT).[2] In contrast to CFPP, LTFT uses a slow constant cooling rate of 1°C/hour. This rate was chosen to mimic the temperature behavior of fuel in the tank of a diesel truck left overnight in a cold environment with its engine turned off. LTFT has been found to correlate well with low temperature operability field tests. However, because of the slow cooling rate, LTFT requires 12 to 24 hours to complete, making the method impractical for routine fuel testing.

While D 975 does not include a low temperature operability requirement, it offers a guideline that "satisfactory operation should be achieved in most cases if the cloud point … is specified at 6°C above the tenth percentile minimum ambient temperature for the area …" This guideline currently is under review. In addition, there have been ongoing discussions in the industry about using the CFPP or LTFT test. Eventually, some dynamic test probably will be used in the U.S. to predict the low temperature flow properties of diesel fuel.

Lubricity There is no doubt that lubricity is an important property of diesel fuel performance. A single tankful of fuel with extremely low lubricity can cause a fuel pump to fail catastrophically. Setting a lubricity requirement to prevent catastrophic failure is relatively easy; setting a requirement to avoid excessive fuel system wear is much harder.

There are three ways to evaluate the lubricity of a fuel. In order of decreasing accuracy and increasing simplicity, they are:

- A vehicle test
- A fuel injection equipment bench test
- A laboratory lubricity test

Vehicle tests require a lot of fuel and a lot of time and effort. They are usually reserved for basic studies of fuel performance. Fuel injection equipment bench tests, such as those designed by Bosch and Stanadyne, require 50 to 100 gallons of sample and 500 to 1000 hours of operating time. Since these tests have not been standardized, the criteria for a pass are not well defined.

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[1] Institute of Petroleum (IP) test method 309.

[2] ASTM D 4539.

Two laboratory lubricity tests have recently been standardized by ASTM: the *Scuffing Load Ball-On-Cylinder Lubricity Evaluator* method (SLBOCLE)[3] and the *High-Frequency Reciprocating Rig* method (HFRR).[4] These tests are relatively quick, inexpensive, and easy to perform.

A lot of work has been done in the past few years to correlate these laboratory tests with field performance. Some SLBOCLE studies indicate that fuels with values below 2,000 g usually will cause accelerated wear in rotary-type fuel injection pumps, and fuels with values above 2,800 g usually will perform satisfactorily. It should be noted that the SLBOCLE test can indicate that fuels treated with an effective lubricity additive have poor lubricity, while the more accurate fuel injection equipment bench test rates them acceptable.

Some HFRR studies indicate that fuels with up to 450-micron wear scar diameters at 60°C (380-micron at 25°C) will perform satisfactorily in all fuel injection equipment. However, other studies show that some fuels and fuel/additive combinations with values above this level still do not cause excessive wear.

ASTM has not yet included a lubricity specification in D 975 because:

- The correlations among results of the two test methods and performance in fuel injection equipment needs further clarification.
- In their current form, both tests methods do not properly rank all fuel/additive combinations.
- The precision of both test methods is poor.

TEST METHODS

ASTM will not adopt a requirement for a property until a standard test method has been developed to measure that property. The test method development process starts with a technical review of the proposed method. Next an interlaboratory test protocol *(round robin)* is conducted in which a common set of samples is sent to a group of labs, which independently analyze them. The results from the participating laboratories are compiled and statistically reviewed. If the agreement among labs is acceptable, a precision statement is developed that gives the acceptable difference between results obtained by different labs on the same sample *(reproducibility)*.

Many of the ASTM test methods were developed in the 1920s, 30s, and 40s; however, test methods based on new technology are continually being adopted. To be sure they remain up to date, ASTM requires each test method to be reviewed every five years and either reapproved, revised, or canceled. The year of last review is attached to the test method number by a hyphen. For example, D 86-96, *Standard Test Method for Distillation of Petroleum Products*, was originally published as a tentative method in 1921, but last reviewed in 1996.

[3] ASTM D 6078

[4] ASTM D 6079.

Cetane Number

ASTM D 613 – *Standard Test Method for Cetane Number of Diesel Fuel Oil*

The cetane number test method for diesel fuel was developed in the 1930s by the Cooperative Fuel Research (CFR) committee and later standardized by ASTM. The method involves running the fuel in a single cylinder engine with a continuously variable compression ratio under a fixed set of conditions. Although the method has been updated over the years, it is still based on the original engine design.

Two specific hydrocarbons were chosen to define the cetane number scale: 1-methylnaphthalene (also called a-*methylnaphthalene*), which burns poorly in a diesel engine, was assigned a cetane number of zero and n-hexadecane *(cetane)*, which burns well, was assigned a cetane number of 100. These hydrocarbons are the *primary reference fuels* for the method.

The cetane number of a fuel is defined as the volume percent of n-hexadecane in a blend of n-hexadecane and 1-methylnaphthalene that gives the same ignition delay period as the test sample. For example, a fuel with a cetane number of 40 will perform the same in the engine as a blend of 40% n-hexadecane and 60% 1-methylnaphthalene.

In 1962, the low cetane number primary reference fuel was replaced with 2,2,4,4,6,8,8-heptamethylnonane (sometimes called *isocetane*). The change was made because 1-methylnaphthalene had been found to be somewhat unstable, expensive, and difficult to use in the CFR engine. When measured against the two original primary standards, 2,2,4,4,6,8,8-heptamethylnonane has a cetane number of 15. When the low cetane number primary reference fuel was changed, the equation used to calculate cetane number was modified to keep the cetane number scale the same.

In day-to-day operations, two secondary reference fuels replace the two primary reference fuels. These fuels are prepared periodically in large volume and made available to testing labs. Their cetane numbers are determined by calibrating them against the primary reference fuels. The work is done by the many labs that are members of the ASTM Diesel National Exchange Group.

Cetane Index

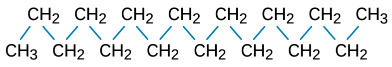
ASTM D 976 – *Calculated Cetane Index of Distillate Fuels*
ASTM D 4737 – *Calculated Cetane Index by Four Variable Equation*

Since measuring cetane numbers requires acquiring and maintaining a cetane number engine, it is apparent that this is a difficult and expensive test. There have been many attempts to develop methods to estimate the cetane number of a fuel for situations in which an engine is not available or the amount of fuel is insufficient for the engine test. To differentiate them from the engine test, these estimates are called *cetane indexes.*

CETANE NUMBER AND OCTANE NUMBER

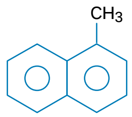
Cetane number (diesel fuel) and octane number (gasoline) both measure the tendency of the fuel to ignite spontaneously. In the cetane number scale, high values represent fuels that ignite readily and, therefore, perform better in a diesel engine. In the octane number scale, high values represent fuels that resist spontaneous ignition and, therefore, have less tendency to knock in a gasoline engine. Because both scales were developed so that higher numbers represent higher quality for the respective use, high cetane number fuels have low octane numbers, and vice versa.

n-Hexadecane



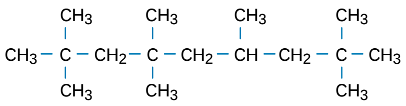
Hexadecane (cetane), cetane number = 100

1-Methylnaphthalene



1-Methylnaphthalene, cetane number = 0

Heptamethylnonane



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3$$

2,2,4,4,6,8,8-Heptamethylnonane (Isocetane), cetane number = 15

D 976 uses the density of the fuel and its mid-distillation temperature to estimate the cetane number. An improved method, D 4737, uses the density of the fuel and the distillation temperatures at 10% vol, 50% vol and 90% vol recovery to estimate the cetane number *(see Figure 5-6)*.

There are other cetane index methods based on other physical, chromatographic, or spectroscopic properties of the fuel, but they are not widely used.

Cetane indexes estimate the “natural” cetane number of the fuel. Since the calculations involve bulk fuel properties, cetane indexes are not affected by the presence of cetane number improvers (diesel ignition improvers). These additives increase the cetane number of a fuel, but do not change its cetane index.

Figure 5-6

Equation Used to Calculate the Cetane Index of a Diesel Fuel in ASTM D 4737

$$\mathrm{CCI} = 45.2 + (0.0892)(T_{10N}) + [0.131 + (0.901)(B)][T_{50N}] + [0.0523 - (0.420)(B)][T_{90N}] + [0.00049][(T_{10N})^2 - (T_{90N})^2] + (107)(B) + (60)(B^2)$$

Where:

CCI = Calculated Cetane Index

D = Density at 15°C

DN = D – 0.85

B = $[e^{(-3.5)(DN)}] - 1$

T_{10} = 10% recovery temperature as measured by D 86 in °C

T_{10N} = $T_{10} - 215$

T_{50} = 50% recovery temperature as measured by D 86 in °C

T_{50N} = $T_{50} - 260$

T_{90} = 90% recovery temperature as measured by D 86 in °C

T_{90N} = $T_{90} - 310$

Figure 5-7 lists the other test methods used to evaluate diesel fuel quality.

Figure 5-7
Other Test Methods for Diesel Fuels

Property	Test Method	Description
Flash Point	ASTM D 93 – *Flash-Point by Pensky-Martens Closed Cup Tester*	The sample is stirred and heated at a slow, constant rate in a closed cup. At intervals, the cup is opened and an ignition source is moved over the top of the cup. The flash point is the lowest temperature at which the application of the ignition source causes the vapors above the liquid to ignite.
Water and Sediment	ASTM D 2709 – *Water and Sediment in Middle Distillate Fuels by Centrifuge*	Water and sediment are contaminants. In this test, a 100 ml sample is centrifuged under specified conditions in a calibrated tube. The amount of sediment and water that settles to the bottom of the tube is read directly using the scale on the tube.
Distillation	ASTM D 86 – *Distillation of Petroleum Products*	The distillation profile is a fundamental fuel property. In this test, a 100 ml sample is placed in a round bottom flask and heated to obtain a controlled rate of evaporation. The temperature is recorded when the first drop is collected (the *initial boiling point*), at recovered volume percentages of 5%, 10%, every subsequent 10% to 90%, 95%, and at the end of the test *(end point)*.
Viscosity	ASTM D 445 – *Kinematic Viscosity of Transparent and Opaque Liquids*	The sample is placed in a calibrated capillary glass viscometer tube and held at a closely controlled temperature. The time required for a specific volume of the sample to flow through the capillary under gravity is measured. This time is proportional to the kinematic viscosity of the sample.
Ash	ASTM D 482 – *Ash from Petroleum Products*	The sample is placed in a crucible, ignited, and allowed to burn. The carbonaceous residue is heated further in a muffle furnace to convert all the carbon to carbon dioxide and all the mineral salts to oxides *(ash)*. The ash is then cooled and weighed.
Sulfur	ASTM D 2622 – *Sulfur in Petroleum Products by X-Ray Spectrometry*	The sample is placed in an x-ray beam and the intensity of the sulfur x-ray fluorescence is measured.
Copper Strip Corrosion	ASTM D 130 – *Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test*	A polished copper strip is immersed in the sample for three hours at 122°F (50°C) and then removed and washed. The condition of the copper surface is qualitatively rated by comparing it to standards.
Hydrocarbon Types	ASTM D 1319 – *Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption*	A small amount of sample is placed at the top of a special glass adsorption column packed with activated silica gel. The top layer of the silica gel in the column has been treated with fluorescent dyes. Isopropyl alcohol is used to transport the sample and the fluorescent dyes down the column. Hydrocarbons are separated into bands of aromatics, olefins, and saturates according to their affinity for the silica gel. The fluorescent dyes are also selectively separated and make the boundaries of the aromatic, olefin, and saturate zones visible under ultraviolet light.

Property	Test Method	Description
Aromaticity	ASTM D 5186 – *Determination of Aromatic Content of Diesel Fuels by Supercritical Fluid Chromatography*	The sample is chromatographed on silica gel using supercritical carbon dioxide as the mobile phase to separate the aromatics from the rest of the sample and to separate the aromatics into monoaromatics and polycyclic aromatics.
Carbon Residue	ASTM D 524 – *Ramsbottom Carbon Residue of Petroleum Products*	The sample is first distilled (D 86) until 90% of the sample has been recovered. The residue is weighed into a special glass bulb and heated in a furnace to 1022°F (550°C). Most of the sample evaporates or decomposes under these conditions. The bulb is cooled and the residue is weighed.
Cloud Point	ASTM D 2500 – *Cloud Point of Petroleum Products*	A clean clear sample is cooled at a specified rate and examined periodically. The temperature at which a haze is first observed is the cloud point.
Pour Point	ASTM D 97 – *Pour Point of Petroleum Products*	A clean sample is first warmed and then cooled at a specified rate and observed at intervals of 5°F (3°C). The lowest temperature at which sample movement is observed when the sample container is tilted is the pour point.
Low Temperature Operability	IP 309 – *Cold Filter Plugging Point of Distillate Fuels (CFPP)*	A sample is cooled at a rate of about 40°C per hour. The highest temperature at which 20 ml of the fuel fails to pass through a 45-micron wire mesh under 2 kPa vacuum in less than 60 seconds is the CFPP.
Low Temperature Operability	ASTM D 4539 – *Filterability of Diesel Fuels by Low-Temperature Flow Test (LTFT)*	A sample is cooled at a rate of 1.8°F/hour (1°C/hour) and filtered through a 17-micron screen under 20 kPa vacuum. The minimum temperature at which 180 ml can be filtered in one minute is recorded.
Oxidation Stability	ASTM D 2274 – *Oxidation Stability of Distillate Fuel Oil (Accelerated Method)*	After filtration to remove any particulate contamination, a 350-milliliter sample is transferred to a special glass container and held at 203°F (95°C) for 16 hours while oxygen is bubbled through the sample. At the end of the treatment period, the sample is allowed to cool to room temperature and filtered to collect any insoluble material that formed.
Storage Stability	ASTM D 4625 – *Distillate Fuel Storage Stability at 110°F (43°C)*	After filtration to remove any particulate contamination, separate 400-milliliter portions of the fuel are transferred to glass containers and stored at 110°F (43°C) for periods of 0, 4, 8, 12, 18, and 24 weeks. At the end of its treatment period, each sample is allowed to cool to room temperature and filtered to collect any insoluble material that formed.
Storage Stability	ASTM D 5304 – *Assessing Distillate Fuel Storage Stability by Oxygen Overpressure*	After filtration to remove any particulate contamination, a 100-milliliter sample is placed in a glass container, which is placed in a pressure vessel preheated to 194°F (90°C). The vessel is pressurized with oxygen to 100 psig and then heated in an oven at 194°F for 16 hours. At the end of the treatment period, the sample is allowed to cool to room temperature and filtered to collect any insoluble material that formed.

Property	Test Method	Description
Thermal Stability	Octel/Dupont F21 – *150°C Accelerated Fuel Oil Stability Test*	After filtration to remove any particulate contamination, a 50-milliliter sample is placed in a glass container and aged for either 90 minutes or 180 minutes at 302°F (150°C) with air exposure. At the end of the treatment period, the sample is allowed to cool to room temperature and filtered. The amount of insoluble material collected on the filter pad is estimated by measuring the light reflection of the pad.
Lubricity	ASTM D 6078 – *Evaluating Lubricity of Diesel Fuels by the Scuffing Load Ball-on-Cylinder Lubricity Evaluator (SLBOCLE)*	This test is based on the BOCLE test, but determines the maximum load that can be applied without causing scuffing. A ball-on-cylinder apparatus immersed in the sample is run under a series of loads to closely bracket the highest non-scuffing load the sample can tolerate.
Lubricity	ASTM D 6079 – *Evaluating Lubricity of Diesel Fuels by the High-Frequency Reciprocating Rig (HFRR)*	A hardened steel ball oscillates across a hardened steel plate under a fixed load for 75 minutes. The point of contact between the ball and plate is immersed in the sample. The size of the resulting wear scar on the steel ball is a measure of the sample's lubricity.
Red Dye	ASTM D 6258 – *Determination of Solvent Red 164 Dye Concentration in Diesel Fuels*	Because the natural color of diesel fuels varies from nearly colorless to amber, red dye concentration cannot be measured accurately by simple visible absorption spectroscopy. This method effectively eliminates interference from the background color of the fuel by using the second derivative of the absorption spectrum. The amplitude difference between the second derivative spectrum maximum at 538 nanometers (nm) and the minimum at 561 nm is used to determine red dye concentration.

6 · Diesel Engines

The diesel engine has long been the workhorse of industry. Favored for their high torque output, durability, exceptional fuel economy, and ability to provide power under a wide range of conditions, diesels are dominant in such applications as trucking, construction, farming, and mining, and are used extensively for stationary power generation and marine propulsion.

Diesel engines are similar to gasoline engines in many ways. Both are internal combustion engines and most versions of both use a four-stroke cycle. But there are four fundamental differences:

- The gasoline engine injects fuel to the air as it is drawn into a cylinder. The diesel engine draws air into a cylinder and injects fuel after the air has been compressed.
- The gasoline engine ignites the fuel-air mixture with a spark. The diesel engine relies on high temperature alone for ignition. Since this high temperature is the result of compressing air above the piston as it travels upward, diesel engines are often referred to as compression-ignition engines.
- The power output of a gasoline engine is controlled by a throttle, which varies the amount of fuel-air mixture drawn into a cylinder. A diesel engine does not throttle the intake air; it controls the power output by varying the amount of fuel injected into the air, thereby varying the fuel-air ratio. This is one of the primary reasons why diesel engines are more fuel efficient than spark ignition gasoline engines.
- A gasoline engine runs stoichiometrically – the fuel-air ratio is fixed so that there is just enough air to burn all the fuel. A diesel engine runs lean – there is always more air than is needed to burn the fuel.

The main advantage of a diesel engine is its high thermal efficiency.[1] Diesel engines can achieve thermal efficiencies in excess of 50%. The best gasoline engines are only about 30% to 33% efficient, and then only at wide throttle openings. As a result, diesel engines have better fuel economy than gasoline engines.

FOUR-STROKE CYCLE

By far the most common type of diesel engine used today has reciprocating pistons and uses a four-stroke operating cycle. In the first stroke *(intake stroke),* the intake valve opens while the piston moves down from its highest position in the cylinder (closest to the cylinder head) to its lowest position, drawing

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[1] Thermal efficiency is defined as the amount of work produced by the engine divided by the amount of chemical energy in the fuel that can be released through combustion. This chemical energy is often referred to as *net heating value* or *heat of combustion* of the fuel.

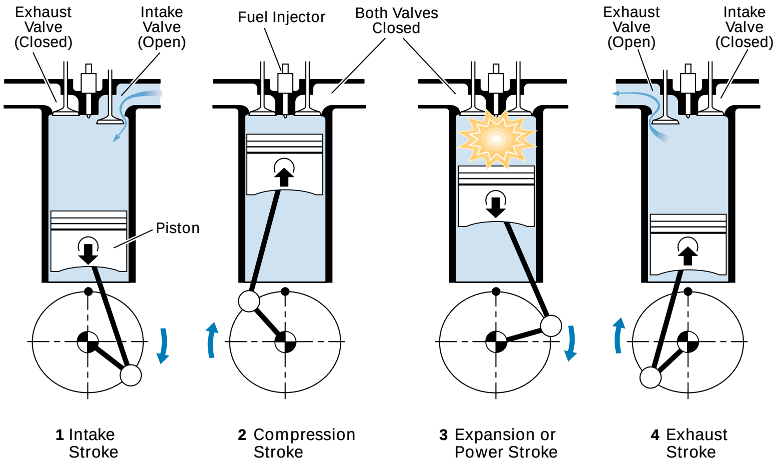
air into the cylinder in the process. In the second stroke *(compression stroke),* the intake valve closes and the piston moves back up the cylinder. This compresses the air and, consequently, heats it to a high temperature, typically in excess of 1000°F (540°C). Near the end of the compression stroke, fuel is injected into the cylinder. After a short delay, the fuel ignites spontaneously, a process called *autoignition.* The hot gases produced by the combustion of the fuel further increase the pressure in the cylinder, forcing the piston down *(expansion stroke or power stroke).* The exhaust valve opens when the piston is again near its lowest position, so that as the piston once more moves to its highest position *(exhaust stroke),* most of the burned gases are forced out of the cylinder.

ENGINE ACRONYMS

The reciprocating piston engine has its own set of acronyms. The position in the cycle when the piston is at the top of its stroke is called *top dead center* (TDC); when it is at its lowest point, it is called *bottom dead center* (BDC). The angle of crankshaft rotation from TDC is expressed in *crank angle degrees* (CAD), with TDC defined as zero degrees. A complete four-stroke cycle involves a crankshaft rotation of 720 CAD, 180 CAD for each stroke. A two-stroke cycle involves a rotation of only 360 CAD. The point of fuel injection is expressed in terms of CAD *before* TDC (BTDC), e.g., 13° BTDC. Valve opening and closing times are also expressed in CAD before or *after* TDC (ATDC).

Figure 6-1

Four-Stroke Cycle



Fuel injection begins shortly before the end of the compression stroke.

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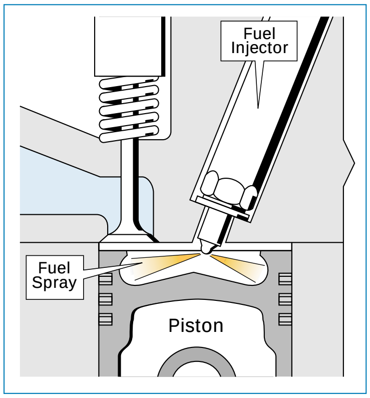
COMPRESSION RATIO

An important parameter of an engine is its compression ratio. This is defined as the ratio of the volume of the cylinder at the beginning of the compression stroke (when the piston is at BDC) to the volume of the cylinder at the end of the compression stroke (when the piston is at TDC). The higher the compression ratio, the higher the air temperature in the cylinder at the end of the compression stroke. Higher compression ratios, to a point, lead to higher thermal efficiencies and better fuel economies. Diesel engines need high compression ratios to generate the high temperatures required for fuel autoignition. In contrast, gasoline engines use lower compression ratios in order to avoid fuel autoignition, which manifests itself as engine knock, often heard as a pinging sound.

FUEL INJECTION

Figure 6-2

Direct-Injection (DI) Process



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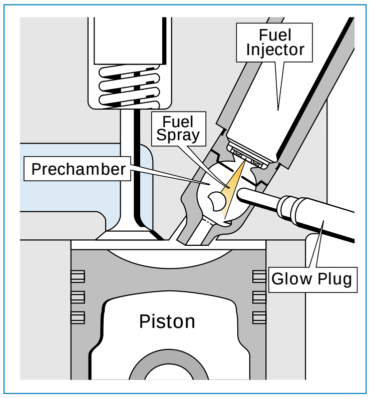
As described above, liquid fuel is injected into the hot, compressed air late in the compression stroke, shortly before the piston reaches TDC. This fuel must vaporize and mix with the air in order to burn. Complete mixing is essential for complete combustion; any fuel that does not burn completely will contribute to hydrocarbon and particulate emissions. The quantity of fuel injected into the cylinder must be less than stoichiometric because complete mixing of all fuel and air in the cylinder can never be totally achieved – it is limited by the amount of air present and the effectiveness of the mixing processes. Diesel engines are typically controlled to a maximum fuel-air ratio to limit the amount of particulate emissions *(smoke limit)* produced by the engine. However, this control also limits the power output of the engine.

Fuel is injected under high pressure (up to 30,000 psi [200 MPa]) into the combustion chamber through a fine nozzle. The injection system is designed to produce a fine spray of small fuel droplets that will evaporate quickly in order to facilitate rapid mixing of fuel vapor and air. Other design features that facilitate mixing include optimizing the position and angle of the nozzle in the cylinder head, and sculpting the piston tops and intake ports to generate a swirling motion of the gases in the cylinder.

DIRECT-INJECTION AND INDIRECT-INJECTION

Figure 6-3

Indirect-Injection (IDI) Process



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The two fuel injection processes used in diesel engines, *direct-injection* (DI) and *indirect-injection* (IDI), are illustrated in Figures 6-2 and 6-3. In a DI engine, fuel is injected directly into the cylinder above the piston. In an IDI engine, fuel is injected into a small *prechamber* connected to the cylinder via a narrow passage that enters the prechamber tangentially. During the compression process, air is forced through this passage, generating a vigorous swirling motion in the prechamber. Then fuel is injected into the prechamber and ignition occurs there. The combination of rapidly swirling air in the prechamber and the jet-like expansion of combustion gases from the prechamber into the cylinder enhances the mixing and combustion of the fuel and air.

The more rapid mixing of fuel and air achieved in IDI engines comes at a price, however. The high velocity flow of air through the narrow passage connecting the main cylinder to the prechamber, as well as the vigorous swirling motion in the prechamber itself, causes the air to lose significantly more heat during compression than it does in a DI engine. Coupled with a pressure drop from the main chamber to the prechamber, this results in an air temperature in the prechamber after compression that is lower than that in a similar DI engine.

Since rapid fuel autoignition requires a certain air temperature, an IDI engine needs a higher compression ratio to achieve the desired air temperature in the prechamber. IDI engines operate at compression ratios of about 20:1 to 24:1; while DI engines operate at ratios of about 15:1 to 18:1. The heat losses that necessitate these higher compression ratios have another, more important effect: they decrease the efficiency of the engine. IDI engines typically achieve fuel efficiencies that are 10% to 20% lower, on a relative basis, than comparable DI engines.

Even with the higher compression ratios, IDI engines may still be hard to start. Most IDI engines use glow plugs to heat the air in the prechamber in order to make starting easier. Glow plugs, which are small resistive heaters, are usually powered for only the first few minutes of engine operation.

With the negative attributes of harder starting and lower efficiency, one may wonder why IDI diesel engines are used at all. The answer is engine speed. As an engine gets smaller, generally it must operate at higher speeds to generate the desired power. As engine speed increases, there is less time *per engine cycle* to inject, vaporize, mix, and combust the fuel. As a result, the higher mixing rates afforded by IDI designs become necessary to achieve good combustion at higher engine speeds. IDI diesels most commonly are used in smaller automotive and light duty truck applications.

TURBOCHARGING, SUPERCHARGING, AND CHARGE COOLING

Since the power output of diesel engines (or for that matter, gasoline engines) is limited by the amount of air they take in, it is common practice to employ some form of forced air induction to increase maximum power. In turbocharging or supercharging, a compressor is used to raise the pressure and, therefore, the density of the air entering the engine. Increasing the total mass of air inducted per cycle allows more fuel to be injected and burned without increasing the fuel-air ratio to the point that particulate emissions become excessive *(smoke limit)*.

Even at equal power, a forced-air diesel engine has an advantage over a naturally aspirated engine. The increased air mass decreases the fuel-air ratio and, thereby improves the engine’s thermal efficiency (fuel economy). In addition, the decrease in fuel-air ratio at part power can also improve emissions performance, depending on other factors.

Turbocharging uses a small exhaust gas driven turbine to drive a similarly small compressor located on the same shaft to pressurize the intake air. Thus, the energy for compressing the intake air is scavenged from the exhaust. Turbocharging has two disadvantages: first, there can be a lag *(turbo lag)* between the time that the driver demands more power and the time when the intake air pressure reaches its maximum; second, turbochargers must operate at high temperatures and high rotational speeds. Appropriate design, combined with the typical operating conditions of most diesel engines, has almost eliminated these mechanical concerns.

Supercharging uses a mechanically driven pump to pressurize the intake air. Several types of pumps are commonly employed; almost all are positive displacement pumps and all are driven by the engine crankshaft, either directly or via gears or belts. Like turbocharging, supercharging can improve thermal efficiency, as well as boost power output. However, because supercharging uses work from the crankshaft to power the compressor, the degree of compression depends upon engine speed, instead of engine load (power output), so there is no power lag as there can be with a turbocharger.

Since both turbocharging and supercharging compress the intake air, they increase its temperature, as well as its density. This temperature increase is counterproductive, because air density is inversely proportional to temperature, that is, the hotter the air, the less dense. An additional increase in density can be achieved by cooling the hot compressed air before it enters the engine. *Charge cooling,* also referred to as *intercooling* or *aftercooling,* passes the hot compressed air coming from the compressor over a heat exchanger (such as a radiator) to lower its temperature. Charge cooling can provide significant gains in power output. It also can decrease NO_X emissions *(see page 53).*

ELECTRONIC ENGINE CONTROLS

Better control of the combustion process is the only way modern diesel engines can meet the demands of high power output, fuel economy, durability, and low levels of emissions. In a diesel engine, this means controlling both the amount of fuel that is injected during each engine cycle and the rate at which it is injected.

Historically, diesel engines have employed mechanical systems to inject fuel into the combustion chamber. While mechanical injectors effectively achieve the required high injection pressures at reasonable cost, they operate in a fixed, predetermined way. Thus, they are not easily adaptable to modern methods of control.

Currently, electronic engine controls and electronic injectors are being used to control fuel injection more carefully. These systems employ a variety of sensors to monitor how the engine is operating by measuring such variables as: engine speed, load demand (“throttle” position), engine coolant and exhaust temperatures, and air temperature and pressure (or mass flow rate). A microprocessor interprets the sensor outputs and generates signals to operate the electronic fuel injectors. In this way, both the total quantity of fuel and the rate at which it is injected (the injection profile) are optimized for the instantaneous engine conditions.

Electronic engine controls are more expensive than traditional mechanical injection systems. Fortunately, the rapid evolution of microprocessors has made it possible to produce high powered systems at an acceptable cost. In many cases, the initial cost of electronic engine control will be more than offset by the savings from increased fuel efficiency.

TWO–STROKE CYCLE

Two-stroke cycle diesel engines are very similar to four-stroke cycle engines, except that they do not have separate intake and exhaust strokes. Instead, exhaust occurs at the end of the expansion, or power, stroke and continues into the early part of the compression stroke. Intake occurs during the end of the expansion stroke and the early part of the compression stroke. To assist the intake process, the intake air is almost always boosted above atmospheric pressure, using supercharging or turbocharging. Air flow into the cylinder and exhaust gas flow out of the cylinder are controlled by conventional poppet valves in the cylinder head, ports in the cylinder wall, or a combination of both.

The advantage of the two-stroke cycle is that it generates more power for a given engine size, since power is generated on every other stroke, rather than every fourth stroke. The disadvantages are that emissions are higher with a two-stroke cycle than with a four-stroke cycle, and that fuel efficiency can be marginally poorer. At one time two-stroke cycle diesel engines were very popular due to their high power density. Their popularity has diminished for the many uses where low emissions are important. However, they are still common in uses such as large marine engines, where poor emissions performance is not currently an issue.

MARINE DIESEL ENGINES

Large marine diesels operate on the same principles as automotive DI diesels, but on a much larger scale. The pistons can be three feet (one meter) in diameter with a six-foot (two-meter) stroke. Because of the high mechanical stress involved with moving the large pistons, they operate at lower speeds, 70-100 rpm. Due to the slow speeds, these engines do not usually employ methods such as swirl to enhance mixing of fuel and air, as they are not necessary. These engines typically have compression ratios of 10:1 to 12:1 and can have thermal efficiencies of up to 55%.

DIESEL ENGINES AND EMISSIONS

Exhaust emissions are the Achilles' heel of diesel engines. Diesel exhaust tends to be high in NO_X and particulates, both visible (smoke) and invisible. Both NO_X and particulates are significant environmental pollutants. Unlike the exhaust of gasoline engines, diesel exhaust contains much less unburned or partially burned hydrocarbons and carbon monoxide. Because of the importance of diesel emissions, it is worth while taking a closer look at the combustion process to see how they are formed. Since the physical and chemical processes taking place in a cylinder during combustion are very complex – and not completely understood – this discussion is necessarily superficial.

As fuel is injected into a cylinder under high pressure, it atomizes into small droplets and begins to evaporate as it moves away from the nozzle. The fuel-air ratio at any point in the cylinder may range from zero, at a point with no fuel, to infinity, inside a fuel droplet that has not yet vaporized. In general, the fuel-air ratio is high near the nozzle tip and low away from it, but because of the complexity of the mixing process, the fuel-air ratio does not change uniformly within the cylinder. Combustion can only occur within a certain range of the fuel-air ratio; if the ratio is too low, there is not enough fuel to support combustion, and if the ratio is too high, there is not enough air.

As the fuel vaporizes into the hot air, it starts to oxidize. As more fuel vaporizes and mixes with air, the number and rate of the oxidation reactions increase until the end of the ignition delay period, when ignition occurs at many locations independently and combustion propagates very rapidly in regions which have fuel-air ratios in the combustible range. This initial combustion after ignition is called the *pre-mixed combustion phase;* it consumes only about 5% to 10% of the fuel used by the engine at typical full-load operation.

At the end of the pre-mixed combustion phase, most of the fuel has yet to be injected or is still in a region that is too rich to burn. But injection continues and fuel continues to vaporize and mix with air, aided by the heat release and turbulence generated by the initial combustion. This quickly generates more gas with the required fuel-air ratio and combustion continues. This is called the *diffusion controlled* or *mixing controlled phase* of combustion and, ideally, consumes all of the remaining fuel.

With this background, we can better understand how pollutants are formed during combustion in a diesel engine. NO_X, hydrocarbons, CO, and particulates are all formed under different conditions and via different mechanisms.

Nitrogen Oxides NO and NO_2 tend to be formed in the stoichiometric and slightly lean regions where there is excess oxygen and the temperature is high. Outside of these regions, either there is insufficient oxygen to form NO_X or temperatures are too low for the reactions to occur quickly enough.

Hydrocarbons HC emissions can be either unburned or partially burned fuel molecules, and can come from several sources. At ignition, some of the vaporized fuel will already be in a region that is too lean for it to burn; and unless it burns later in the cycle, this fuel will be emitted. The cylinder walls and “crevice” regions around the top of the piston edge and above the rings are much cooler than the combustion gases and tend to quench flames as they encroach. Thus, fuel at the cylinder wall can contribute to HC emissions. Fuel that does not vaporize during a cold start makes up the white smoke seen under this condition. A small amount of fuel can also dissolve in the thin film of lubricating oil on the cylinder wall, be desorbed in the expansion stroke, and then emitted. However, since diesel engines operate at an overall lean fuel-air ratio, they tend to emit low levels of hydrocarbons.

Carbon Monoxide CO is a result of incomplete combustion and is formed mostly in those regions of the cylinder that are too fuel-rich to support complete combustion, although it may also originate at the lean limit of combustible fuel-air mixtures. If temperatures are high enough, the CO can further react with oxygen to form CO_2. Because diesel engines have excess oxygen, CO emissions are generally low.

Particulates Some of the fuel droplets may never vaporize, and thus, never burn. But the fuel doesn’t remain unchanged; the high temperatures in the cylinder cause it to decompose. Later, these droplets may be partly or completely burned in the turbulent flame. If they are not completely burned, they will be emitted as droplets of heavy liquid or particles of carbonaceous material. The conversion of fuel to particulates is most likely to occur when the last bit of fuel is injected in a cycle, or when the engine is being operated at high load and high speed. At higher engine speeds and loads, the total amount of fuel injected increases and the time available for combustion decreases. Also, some of the lubricating oil on the cylinder wall is partially burned and contributes to particulate emissions. Finally, a poorly operating or mistimed fuel injection system can substantially increase emissions of particulates.

EMISSION REDUCTION TECHNOLOGIES

In recent years improvements in engine technology have led to a large reduction in emissions *(see Chapter 3)*. A modern diesel engine that has been well maintained emits much less smoke and other pollutants than older engines. This section will look at some of the approaches taken to reduce diesel engine emissions.

The design of the combustion system is the most important factor in determining emissions. Fuel plays a secondary, but still significant, role. There have been many advances in combustion system design in recent years that have led to a reduction in emissions including:

- **Higher Injection Pressures** This leads to better atomization and smaller fuel droplets, which vaporize more readily than larger droplets.
- **Careful Injection Targeting** The position and angle of the injector in the cylinder head and the design of the nozzle are optimized to minimize emissions.
- **Charge Shaping** The rate of fuel *(charge)* injection can be controlled deliberately *(shaped)* during injection to achieve desired effects. For example, a small amount of fuel can be injected early and allowed to ignite before the rest of the charge is injected. Early injection acts like a pilot light for the main injection. Other strategies are also used; they are optimized for each engine design.
- **More Air Motion** The cylinder head, air intake valve, and piston head are designed to provide optimal air motion for better fuel-air mixing.
- **Charge Cooling** (Forced Air Induction Engines) As described earlier, most diesel engines employ supercharging or turbocharging in order to increase the maximum power. In these designs, an engine driven or exhaust driven pump is used to force more air into the cylinders by compressing it. Compressing or pressurizing the intake air also heats it. Since NO_X formation is very sensitive to temperature, this also tends to increase NO_X emissions. However, this effect can be mitigated by cooling the intake air by passing it over a heat exchanger after it has been compressed by the supercharger or turbocharger, but before it enters the engine cylinder.
- **Lower Oil Consumption** Diesel engines partially burn some of the crankcase lubricating oil that seeps past the piston rings into the combustion chamber. New designs minimize this effect.
- **Exhaust Gas Recirculation (EGR)** As mentioned above, the formation of NO_X is strongly affected by the temperature in the combustion chamber. This temperature can be reduced somewhat by diluting the reaction mixture with an inert gas. Since some of the heat generated by combustion must be used to heat this inert gas, the maximum temperature of the combustion gas is reduced. Since engine exhaust is essentially inert, it can be used for this purpose. EGR circulates a portion of the exhaust gas back to the air intake manifold. The reduction in NO_X is accompanied by a small loss of power.

Besides these changes designed to minimize the production of pollutants, there are also systems designed to remove pollutants from the exhaust gas.

Particulate traps filter the exhaust gas before it is released to the atmosphere. Many different designs have been tested and particulate reductions of up to 60% have been achieved. Research is underway to design systems that will capture even more of the particulates.

Of course, the particulates build up in the traps over time and must be removed. This is achieved by burning, since they are mainly carbon. Some designs use electrical resistance heaters to raise the temperature in the trap high enough to burn off the particulates, others have built a burner into the trap, and a new design uses microwave energy. In one system, a catalyst is used to lower the regeneration temperature. Research is underway to achieve more effective and more easily regenerated traps.

Catalytic converters can be used to remove pollutants from diesel exhaust. Oxidation catalysts, similar to those used in gasoline cars, convert unburned hydrocarbons and carbon monoxide to carbon dioxide and water. These converters are not as effective as the ones in gasoline vehicles. Sulfur from the fuel tends to deactivate the catalyst, and the particulates in the exhaust gas build up on the catalyst and physically block the exhaust gases from the catalyst's surface. The cooler temperature of diesel engine exhaust, compared to gasoline engine exhaust, also reduces catalyst efficiency. Fortunately, hydrocarbon and carbon monoxide emissions from diesel engines are inherently low, so after treatment to remove these pollutants is rarely needed.

Probably the biggest emissions challenge for designers of diesel engines is reducing NO_X emissions. The high combustion temperatures in a diesel engine favor NO_X formation. EGR can be used to lower NO_X formation, but removing NO_X from exhaust gases involves reducing it to diatomic nitrogen (N_2). This is a challenge because the excess oxygen in diesel exhaust makes it an oxidizing environment. Oxidation and reduction are opposing chemical tendencies; conditions that favor oxidation are generally unfavorable to reduction. The development of a "lean NO_X" catalyst, one that will reduce NO_X in a lean, or excess-oxygen environment, is an area of active research.

Another approach to converting NO_X to nitrogen is *selective catalytic reduction* (SCR). In SCR, a reduced nitrogen compound, usually ammonia or urea, is injected into the exhaust gas in an amount proportional to the NO_X present. The NO_X and the reduced nitrogen compound react in the presence of a catalyst to form nitrogen and water. SCR has been successful in reducing NO_X from stationary sources, but is more difficult to implement in a vehicle.

7 · Diesel Fuel Additives

The first part of this chapter describes the additives that are used in diesel fuel – what they are and why and how they work. The second part describes their use in practice.

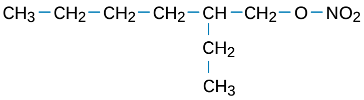
TYPES OF ADDITIVES

Diesel fuel additives are used for a wide variety of purposes, however they can be grouped into four major categories:

- Engine performance
- Fuel handling
- Fuel stability
- Contaminant control

Engine Performance Additives This class of additives can improve engine performance. The effects of different members of the class are seen in different time frames. Any benefit provided by a *cetane number improver* is immediate, whereas that provided by *detergent additives* or *lubricity additives* is typically seen over the long term, often measured in tens of thousands of miles.

Cetane Number Improver



$$CH_3-CH_2-CH_2-CH_2-\underset{\substack{|\\ CH_2\\ |\\ CH_3}}{CH}-CH_2-O-NO_2$$

2-Ethylhexyl nitrate

Cetane Number Improvers (Diesel Ignition Improvers) Cetane number improvers can reduce combustion noise and smoke. The magnitude of the benefit varies among engine designs and operating modes, ranging from no effect to readily perceptible improvement.

2-Ethylhexyl nitrate (EHN) is the most widely used cetane number improver. It is sometimes also called *octyl nitrate.* EHN is thermally unstable and decomposes rapidly at the high temperatures in the combustion chamber. The products of decomposition help initiate fuel combustion and, thus, shorten the ignition delay period from that of the fuel without the additive.

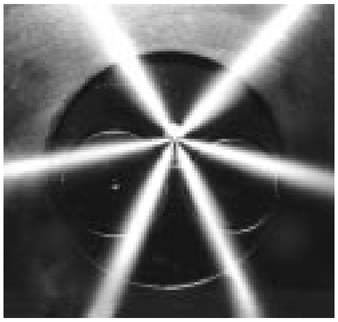
The increase in cetane number from a given concentration of EHN varies from one fuel to another. It is greater for a fuel whose natural cetane number is already relatively high. The incremental increase gets smaller as more EHN is added, so there is little benefit to exceeding a certain concentration. EHN typically is used in the concentration range of 0.05% mass to 0.4% mass and may yield a 3 to 8 cetane number benefit.

Other alkyl nitrates, as well as ether nitrates and some nitroso compounds, also have been found to be effective cetane number improvers, but they are not currently used commercially. Di-tertiary butyl peroxide was recently introduced as a commercial cetane number improver.

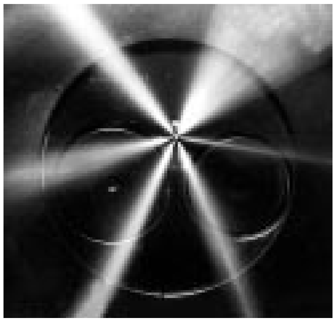
A disadvantage of EHN is that it decreases the thermal stability of some fuels. The effect of the other cetane number improvers on thermal stability is unknown, but it seems likely that they will be similarly disadvantaged. Several laboratories are investigating this issue.

Injector Cleanliness Additives Fuel and/or crankcase lubricant can form deposits in the nozzle area of injectors – the area exposed to high cylinder temperatures. The extent of deposit formation varies with engine design, fuel composition, lubricant composition, and operating conditions. Excessive deposits may upset the injector spray pattern *(see Figure 7-1)* which, in turn, may hinder the fuel-air mixing process. In some engines, this may result in decreased fuel economy and increased emissions.

Figure 7-1
Fuel Spray Patterns



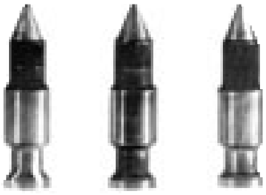
Clean injector – regular spray pattern



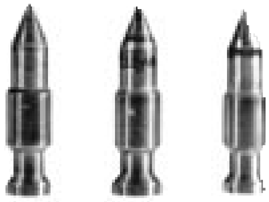
Deposited injector – irregular spray pattern

Ashless polymeric detergent additives can clean up fuel injector deposits and/or keep injectors clean *(see Figure 7-2)*. These additives are composed of a polar group that bonds to deposits and deposit precursors, and a non-polar group that dissolves in the fuel. Thus, the additive can redissolve deposits that already have formed and reduce the opportunity for deposit precursors to form deposits. Detergent additives typically are used in the concentration range of 50 ppm to 300 ppm.

Figure 7-2
Typical Deposit Levels on a Fuel Injector Plunger Susceptible to Deposit Formation



Untreated fuel



Fuel with deposit control additive

Lubricity Additives Lubricity additives are used to compensate for the poor lubricity of severely hydrotreated diesel fuels *(see page 5)*. They contain a polar group that is attracted to metal surfaces, causing the additive to form a thin surface film. The film acts as a boundary lubricant when two metal surfaces come in contact. Two additive chemistries, fatty acids and esters, are commonly used. The fatty acid type is typically used in the concentration range of 10 ppm to 50 ppm. Since esters are less polar, they require a higher concentration range of 50 ppm to 250 ppm.

Smoke Suppressants Some organometallic compounds act as combustion catalysts. Adding these compounds to fuel can reduce the black smoke emissions that result from incomplete combustion. During the 1960s, before the Clean Air Act and the formation of the EPA, certain barium organometallics were used occasionally as smoke suppressants. The EPA subsequently banned them because of the potential health hazard of barium in the exhaust.

Smoke suppressants based on other metals, e.g., iron, cerium, or platinum, are used in other parts of the world; but have not been approved by the EPA for use in the U.S. These additives are often used in vehicles equipped with particulate traps to lower particulate emissions even further.

Fuel Handling Additives

Antifoam Additives Some diesel fuels tend to foam as they are pumped into vehicle tanks. The foaming can interfere with filling the tank completely, or result in a spill. Most antifoam additives are organosilicone compounds and are typically used at concentrations of 10 ppm or lower.

De-Icing Additives Free water in diesel fuel freezes at low temperatures. The resulting ice crystals can plug fuel lines or filters, blocking fuel flow. Low molecular weight alcohols or glycols can be added to diesel fuel to prevent ice formation. The alcohols/glycols preferentially dissolve in the free water, giving the resulting mixture a lower freezing point than that of pure water.

Low Temperature Operability Additives There are additives that can lower a diesel fuel's pour point *(gel point)* or cloud point, or improve its cold flow properties *(see page 38)*. Most of these additives are polymers that interact with the wax crystals that form in diesel fuel when it is cooled below the cloud point *(see sidebar on page 7)*. The polymers mitigate the effect of the wax crystals on fuel flow by modifying their size, shape, and/or degree of agglomeration. The polymer-wax interactions are fairly specific, so a particular additive generally will not perform equally well in all fuels. To be effective, the additives must be blended into the fuel before any wax has formed, i.e., when the fuel is above its cloud point. The best additive and treat rate[1] for a particular fuel can not be predicted; it must be determined experimentally.

The benefits that can be expected from different types of low temperature operability additives are listed in Figure 7-3.

Figure 7-3
Low Temperature Operability Additive Benefits

Additive Type	Typical Treat Rate, ppm	Typical Benefit*	
		°C	°F
Cloud point	200–2000	3–4	5–7
LTFT	50–2000	8–12	15–25
CFPP	100–2000	15–20	25–35
Pour point	100–300	30–40	50–70

* Reduction from value for unadditized fuel.

Drag Reducing Additives Pipeline companies sometimes use drag reducing additives to increase the volume of product they can deliver. These high molecular weight polymers reduce turbulence in fluids flowing in a pipeline, which can increase the maximum flow rate by 20% to 40%. Drag reducing additives are typically used in concentrations below 15 ppm. When the additized product passes through a pump, the additive is broken down *(sheared)* into smaller molecules that have no effect on product performance in engines.

Fuel Stability Additives Fuel instability results in the formation of gums that can lead to injector deposits or particulates that can plug fuel filters or the fuel injection system. The need for a stability additive varies widely from one fuel to another. It depends on how the fuel was made – the crude oil source and the refinery processing and blending. Stability additives typically work by blocking one step in a multi-step reaction pathway *(see page 29)*. Because of the complex chemistry involved, an additive that is effective in one fuel may not work as well in another. If a fuel needs to be stabilized, it should be tested to select an effective additive and treat rate. Best results are obtained when the additive is added immediately after the fuel is manufactured.

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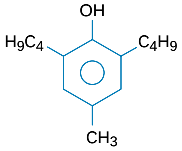
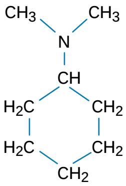
[1] *Treat rate* or *treatment rate* is the concentration of the additive in the fuel.

Antioxidant



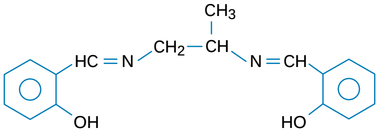
2,6-Di-t-butyl-4-methyl phenol

Stabilizer



N, N-Dimethylcyclohexyl amine

Metal Deactivator



N, N-Disalicylidene-1, 2-propanediamine (DMD)

Antioxidants One mode of fuel instability is oxidation, in which oxygen in the small amount of dissolved air attacks reactive compounds in the fuel. This initial attack sets off complex chain reactions. Antioxidants work by interrupting the chains. Hindered phenols and certain amines, such as phenylenediamine, are the most commonly used antioxidants. They typically are used in the concentration range of 10 ppm to 80 ppm.

Stabilizers Acid-base reactions are another mode of fuel instability. The stabilizers used to prevent these reactions typically are strongly basic amines and are used in the concentration range of 50 ppm to 150 ppm. They react with weakly acidic compounds to form products that remain dissolved in the fuel, but do not react further.

Metal Deactivators When trace amounts of certain metals, especially copper and iron, are dissolved in diesel fuel, they catalyze (accelerate) the reactions involved in fuel instability. Metal deactivators tie up *(chelate)* these metals, neutralizing their catalytic effect. They typically are used in the concentration range of 1 ppm to 15 ppm.

Dispersants Multi-component fuel stabilizer packages may contain a dispersant. The dispersant doesn’t prevent the fuel instability reactions, but it does disperse the particulates that form, preventing them from clustering into aggregates large enough to plug fuel filters or injectors. Dispersants typically are used in the concentration range of 15 ppm to 100 ppm.

Contaminant Control This class of additives mainly is used to deal with housekeeping problems.

Biocides The high temperatures involved in refinery processing effectively sterilize diesel fuel. But the fuel quickly becomes contaminated with microorganisms present in air or water. These microorganisms include bacteria and fungi (yeasts and molds).

Since most microorganisms need free water to grow, biogrowth is usually concentrated at the fuel-water interface, when one exists. In addition to the fuel and water, they also need certain elemental nutrients in order to grow. Of these nutrients, phosphorous is the only one whose concentration might be low enough in a fuel system to limit biogrowth. Higher ambient temperatures also favor growth. Some organisms need air to grow *(aerobic)*, while others only grow in the absence of air *(anaerobic)*.

The time available for growth also is important. A few, or even a few thousand, organisms don’t pose a problem. Only when the colony has had time to grow much larger will it have produced enough acidic by-product to accelerate tank corrosion or enough biomass (microbial slime) to plug filters. Although growth can occur in working fuel tanks, static tanks – where fuel is being stored for an extended period of time – are a much better growth environment when water is present.

Biocides can be used when microorganisms reach problem levels. The best choice is an additive that dissolves in both the fuel and the water so it can attack the microbes in both phases. Biocides typically are used in the concentration range of 200 ppm to 600 ppm.

A biocide may not work if a heavy biofilm has accumulated on the surface of the tank or other equipment, because then it doesn't reach the organisms living deep within the film. In such cases, the tank must be drained and mechanically cleaned.

Even if the biocide effectively stops biogrowth, it still may be necessary to remove the accumulated biomass to avoid filter plugging. Since biocides are toxic, any water bottoms that contain biocides must be disposed of appropriately.

The best approach to microbial contamination is prevention. And the most important preventative step is keeping the amount of water in a fuel storage tank as low as possible, preferably zero.

Demulsifiers Normally, hydrocarbons and water separate rapidly and cleanly. But if the fuel contains polar compounds that behave like surfactants and if free water is present, the fuel and water can form an emulsion. Any operation which subjects the mixture to high shear forces, like pumping the fuel, can stabilize the emulsion. Demulsifiers are surfactants that break up emulsions and allow the fuel and water phases to separate. Demulsifiers typically are used in the concentration range of 5 ppm to 30 ppm.

Corrosion Inhibitors Since most petroleum pipes and tanks are made of steel, the most common corrosion is the formation of rust in the presence of water. Over time, severe rusting can eat holes in steel walls, creating leaks. More immediately, the fuel is contaminated by rust particles, which can plug fuel filters or increase fuel pump and injector wear.

Corrosion inhibitors are compounds that attach to metal surfaces and form a barrier that prevents attack by corrosive agents. They typically are used in the concentration range of 5 ppm to 15 ppm.

USE OF ADDITIVES

Additives may be added to diesel fuel at the refinery, during distribution, or after the fuel has left the terminal. During distribution, additives may be injected prior to pipeline transit (if the fuel is distributed by pipeline), or at the terminal. When the fuel leaves the terminal, its ownership generally transfers from the refiner or marketer to the customer, who may be a reseller *(jobber)* or the ultimate user. For this reason, additives added to the fuel ***after*** it leaves the terminal are called *aftermarket additives.*

Refinery Additization This review discusses the many factors that determine the quality of diesel fuel. Given their number, it must be obvious that the quality of all diesel fuels is not the same. But, since fuel is the single largest operating expense for a diesel truck fleet, many users make their purchase decisions based on price alone.

Refiners have a legal requirement to provide a product that meets specifications. Beyond that, reputable refiners ensure that non-specification properties, such as stability, lubricity, and low temperature operability are suitable for the intended use.

The refiner has several options on how to achieve the desired properties: choice of crude oil, refinery processing, refinery blending, or the use of additives. The balance between refining actions and additive use is driven by economics. Since there are no legal requirements that diesel fuel contain additives, except red dye in high sulfur and tax-exempt fuel *(see page 18)*, some refiners may use no additives at all and still provide a high quality fuel.

There is no published information on use of additives. The following comments represent the authors' impression of common industry practice in the U.S.:

- Pour point reducers are probably the diesel fuel additive most widely used by refiners. However, their use is limited to fuel made in the wintertime and destined for regions with colder ambient temperatures.
- Some refiners add one or more additives to improve fuel stability, either as a regular practice or on an "as needed" basis.
- Some refiners use a cetane number improver when the additive cost is less than the cost of processing to increase cetane number.
- Red dye is added to high sulfur diesel fuel and may be added to tax-exempt diesel fuel at the refinery.

Cloud point is the property used in the U.S. to measure the low temperature operability of diesel fuel. Most refiners control cloud point by processing changes because cloud point reducing additives have historically been relatively ineffective.

While pour point reducers may improve CFPP, U.S. refiners probably don't use additives specifically designed to lower CFPP because it is not a specification property. Since Europe uses CFPP instead of cloud point as a measure of low temperature operability, additives which reduce CFPP are used more widely there.

Antifoam additives are widely used in Europe and Asia to ensure that consumers can fill their cars and trucks without spilling fuel on their hands, clothes, and vehicles. There is less of a problem with fuel foaming in North America because of different fuel properties (lower distillation end point), vehicle tank designs, and fuel dispensing pumps.

California: A Special Case Because of its unique diesel fuel regulations, California is a special case. California regulations restrict the aromatics content of diesel fuel in order to reduce emissions. The regulations can be met either with a low aromatics diesel (LAD) having less than 10% aromatics, or with an alternative low aromatics diesel (ALAD) formulation that gives an equivalent reduction in emissions *(see page 17)*. Many of these ALAD formulations use cetane number improvers to help achieve the necessary emissions reduction. As a result, a significant percentage of the low aromatic diesel fuel now sold in California contains some cetane number improver.[2]

[2] *1996 American Petroleum Institute/National Petroleum Refiners Association Survey of Refining Operations and Product Quality.* Final Report, July 1997.

Reducing diesel aromatic content to 10% requires more severe hydrotreating than reducing sulfur content. As a result, the lubricity of some LAD may be low, so some refiners may treat the fuel with a lubricity additive. (In the rest of the U.S., hydrotreating to remove sulfur may reduce lubricity, but not enough to require a lubricity additive.)

Two diesel fuel lubricity guidelines have recently been proposed in the U.S.: the EMA guideline recommends a 3100 g minimum (SLBOCLE method) and the state of California recommends a 3000 g minimum (SLBOCLE method). There are ongoing discussions and investigations in the industry, which may lead to a specification *(see page 39)*. In the absence of a specification, each refiner sets its own standard.

Distribution System Additization When diesel fuel is distributed by pipeline, the operator may inject corrosion inhibiting and/or drag reducing additives. No additional additives are added to diesel fuel distributed by truck or marine ship or barge.

Some refiners and petroleum marketers offer a premium diesel *(see page 35)*, which can be created at the refinery by the proper choice of operating conditions, or at the terminal by treating regular diesel with additives. Usually a blend of several additives, called an additive package, is used, rather than a single additive. The package may contain: a detergent/dispersant, one or more stabilizing additives, a cetane number improver, a low temperature operability additive (flow improver or pour point reducer), and a biocide. Each refiner or marketer is likely to use a different package of additives and a different treat rate. There are good reasons for this; many additives must be tailored to the fuel in which they will be used and the requirements of the market vary from place to place.

Aftermarket Additives It would be convenient for the user if a finished diesel fuel could satisfy all his or her requirements without the use of supplemental additives. Although this is often the case, some users must use additives because the low temperature conditions in their region are more severe than those for which the fuel was designed, or because of other special circumstances. Other users feel that they need a higher quality diesel than regular diesel. And, finally, there are users who regard the cost of an additive as cheap insurance for their big investment in equipment.

A large number of aftermarket additive products are available to meet these real or perceived needs. Some are aggressively marketed with testimonials and bold performance claims that seem “too good to be true.” So, as with any purchase, it is wise to remember the advice, *caveat emptor* – let the buyer beware.

It may be helpful to regard additives as medicine for fuel. Like medicine, they should be prescribed by an expert who has made an effort to diagnose the problem. And they should be used in accordance with the recommendations of the engine manufacturer and the instructions of the additive supplier. Sometimes indiscriminant use of additives can do more harm than good because of unexpected interactions.

Questions and Answers

The diesel fuel I bought recently has a darker color than I am used to seeing. Does this mean the fuel has gone bad?

The color of a diesel fuel is not related to its performance. As long as the fuel meets the specifications, it will perform well in your engine.

Diesel fuel can range from colorless to an amber or light brown color, depending on the crude oil and the refinery processing used to produce it. Diesel fuel may darken after months of storage, due to oxidation of trace components, but this will not affect its performance. However, if the darkening is accompanied by the formation of sediment, the fuel could plug filters. If diesel fuel is stored for use in an emergency, it should be used within one year and replaced with fresh fuel, unless special precautions are taken.

What special precautions need to be taken with diesel fuel that must be stored for a long period of time?

While storage stability should not be a concern for the majority of diesel fuel users, those who store diesel fuel for a prolonged period, i.e., one year or longer, can take steps to maintain fuel integrity. The actions listed below provide increasing levels of protection:

1. Purchase clean, dry fuel from a reputable supplier. Keep the stored fuel cool and dry. The presence of free water encourages corrosion of metal storage tanks and provides the medium for microbiological growth.
2. Add an appropriate stabilizer that contains an antioxidant, biocide, and corrosion inhibitor.
3. Use a fuel quality management service to regularly test the fuel, and as necessary, *polish* it – by filtration through portable filters – and add fresh stabilizer. This is common practice for nuclear power plants with back-up diesel powered generators.
4. Install a dedicated fuel quality management system that automatically tests and purifies the fuel and injects fresh stabilizer.

Does low sulfur diesel fuel have enough lubricity?

Yes. Even though the process used to lower the sulfur in diesel can also remove some of the components that give the fuel its lubricity, reputable refiners monitor this property and use an additive, as needed, to raise the lubricity to an acceptable level.

Will low sulfur diesel or low aromatics diesel cause fuel system leaks?

The introduction of low sulfur diesel for on-road use in the U.S. was accompanied by fuel system leaks in a very small percentage of vehicles. Investigations into the cause of these leaks suggest that the problem was linked to the change in the aromatics content of the fuel and to seal material and age.

Diesel fuel systems contain “O-rings” and other parts made of elastomeric materials. These elastomers swell slightly when they contact diesel fuel, because they absorb aromatic compounds from the fuel. Exposure to a fuel with a lower aromatics content will result in some of the absorbed aromatics being leached out, causing the elastomer to shrink towards its original size. If the elastomer is still pliable, this shrinkage will not cause a leak. However, if age or service at higher-than-normal temperatures has caused the elastomer to loose its elasticity, a leak could occur. Vehicle owners should be aware that elastomeric parts have finite lives and should be replaced as necessary.

By itself, low sulfur or low aromatics diesel fuel does not cause fuel system leaks. They are caused by the combination of a change from higher to lower aromatics fuel and aged O-rings and elastomeric parts that have lost their elasticity.

I accidentally mixed gasoline with my diesel. What can I do?

One percent or less gasoline will lower the flash point of a gasoline/diesel fuel blend below the specification minimum for diesel fuel. This will not affect the fuel’s engine performance, but it will make the fuel more hazardous to handle. Larger amounts of gasoline will lower the viscosity and/or cetane number of the blend below the specification minimums for diesel fuel. These changes can degrade combustion and increase wear.

The best course of action is to recycle gasoline-contaminated diesel fuel back to your supplier. People ask if they can correct the problem by adding more diesel fuel to the blend. Usually the answer is no; the amount of additional diesel fuel needed to bring the flash point on test is impractically large. Those who try dilution should have the blend checked by a laboratory before use to be sure it meets specifications.

Does diesel fuel plug filters?

There can be several causes of a plugged filter. For example, low temperature can cause wax crystallization, which can lead to filter plugging if summer diesel is used during cold weather. Dirt in the fuel or excessive microbial growth can also cause filter plugging. The latter are “housekeeping” issues and are not directly related to the fuel itself.

Under some circumstances, a fuel with poor thermal stability can plug a filter. When the fuel is exposed to the hot surfaces of the injectors, it forms particulates. If the fuel system is designed to return a significant proportion of the fuel to the fuel tank, the particulates are returned too. When the fuel is recycled, the fuel filter collects some of the particulates. Over time, particulate build up plugs the filter. This problem has been observed for engines that were operating at high load and, therefore, engines that were operating at higher than average temperatures.

What is the Btu content of diesel fuel?

The heating value or energy content is not a product specification for diesel fuel, so it is not measured for each batch. However, the specifications effectively limit the heating value to a relatively narrow range. A typical net heating value for low sulfur No. 2-D fuel is 130,000 Btu per gallon.

How much No. 1-D diesel fuel must I add to No. 2-D diesel fuel to lower the cloud point for winter weather?

The cloud point of No. 2-D is lowered by about 3°F for every 10% volume of No. 1-D in the blend. Lowering the cloud point by 10°F requires the addition of more than 30% volume No. 1-D.

What is the difference between No. 1-D diesel fuel and No. 2-D diesel fuel and can they be used interchangeably?

Always check with the manufacturer about the fuel requirements of your engine. However, both No. 1-D and No. 2-D are intended for use in compression ignition engines. In fact, in cold weather, No. 1-D is blended into No. 2-D or used by itself.

Three of the biggest differences between the two fuels are cetane number, heat content, and viscosity. The cetane number of No. 1-D may be one to two numbers below that of No. 2-D, but still above 40, the required minimum.

Since No. 1-D is less dense then No. 2-D, its heat content, measured in Btu/gallon, will be a few percent lower, leading to a similar reduction in fuel economy.

The lubricity of No. 1-D is likely to be slightly lower than that of No. 2-D because of its lower viscosity. Its lubricity is unlikely to be low enough to cause catastrophic failure. However, a steady diet of No. 1-D in equipment designed for No. 2-D may result in greater long term wear in the fuel delivery system.

Can I get rid of my used engine oil by adding it to diesel fuel?

Adding used engine oil to diesel fuel used to be a common practice. However, it almost certainly results in a blend that does not meet diesel fuel specifications. One or more of these properties may be too high: 90% boiling point, sulfur content, ash, water and sediment, viscosity, and carbon residue. A diesel fuel/used oil blend may not be sold as diesel fuel, and we recommend against using it as a diesel fuel.

In California, addition of used engine oil to diesel fuel is a violation of hazardous waste regulations. Diesel fuel users in other areas who may consider this practice should check for any applicable regulations.

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Reformulated Diesel Fuel

Fuels and Energy Division Office of Mobile Sources
United States Environmental Protection Agency
Mail Code: 6406J
401 M Street SW
Washington, D.C.
(202) 233-9000
http://www.epa.gov/omswww/

California Air Resources Board
P.O. Box 2815
Sacramento, CA 95814
(916) 322-2990
http://www.arb.ca.gov/html/homepage.htm

Federal Regulations

Fuels and Energy Division Office of Mobile Sources
United States Environmental Protection Agency
Mail Code: 6406J
401 M Street SW
Washington, D.C.
(202) 233-9000
http://www.epa.gov/omswww/

Code of Federal Regulations, Title 40 – Protection of Environment

Part 51 – Requirements for Preparation, Adoption, and Submittal of Implementation Plans

Subpart S – Inspection/Maintenance Program Requirements

Part 79 – Registration of Fuels and Fuel Additives

Part 80 – Regulation of Fuels and Fuel Additives

Part 85 – Control of Air Pollution From Motor Vehicles and Motor Vehicle Engines

Part 86 – Control of Air Pollution From New and In-use Motor Vehicles and In-use Motor Vehicle Engines and Test Procedures

National Vehicles and Fuel Emission Laboratory
Office of Mobile Sources
United States Environmental Protection Agency
2565 Plymouth Road
Ann Arbor, Michigan 48105
(313) 668-4200

California Regulations

California Air Resources Board
P.O. Box 2815
Sacramento, CA 95814
(916) 322-2990
http://www.arb.ca.gov/html/homepage.htm

Questions?

Contact Chevron Fuels Technical Service
(510) 242-5357
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Abbreviations

°F	degrees Fahrenheit, the unit of temperature in the U.S. customary system
°C	degrees Celsius, the unit of temperature in the metric (SI) system
°API	degrees API, the unit of gravity in the API system
ALAD	alternative low aromatics diesel
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
BDC	bottom dead center; the position of the piston at the bottom of its stroke
Btu	British thermal unit
CAD	crank angle degrees
CARB	California Air Resources Board
CFPP	cold filter plugging point
CFR	Cooperative Fuel Research
CO	carbon monoxide
CO_2	carbon dioxide
CRC	Coordinating Research Council
cSt	centistoke
DI	direct-injection
EHN	2-ethylhexylnitrate, a cetane number improver
EMA	Engine Manufacturers Association
EPA	U.S. Environmental Protection Agency
FCC	fluid catalytic cracking
g/bhp-hr	grams per brake-horsepower hour
HC	hydrocarbon
HFRR	high frequency reciprocating rig; device for measuring fuel lubricity
IARC	International Agency for Research on Cancer
IDI	indirect-injection
IRS	Internal Revenue Service
ISO	International Standards Organization
kPa	kilo Pascal: a unit of pressure in the metric (SI) system
LAD	low aromatics diesel
LCO	light cycle oil
LTFT	low-temperature flow test
LPG	liquefied petroleum gas
MPa	mega Pascal: a unit of pressure in the metric (SI) system
NAAQS	National Ambient Air Quality Standard
NCWM	National Conference on Weights and Measures
NIOSH	National Institute of Occupational Safety and Health
NMHC	non-methane hydrocarbons
NO	nitric oxide
NO_2	nitrogen dioxide
O_3	ozone
NO_x	nitrogen oxides (or oxides of nitrogen); $NO + NO_2$
PM	particulate matter
PM2.5	particulate matter whose particle size is less than or equal to 2.5 microns
PM10	particulate matter whose particle size is less than or equal to 10 microns
PAH	polycyclic aromatic hydrocarbon
PNA	polynuclear aromatic hydrocarbon
POM	polycyclic organic matter
ppm	parts per million
ptb	pounds per thousand barrels
rpm	revolutions per minute
SAE	Society of Automotive Engineers
SCR	selective catalytic reduction
SIP	State Implementation Plan
SLBOCLE	scuffing load ball-on-cylinder lubricity evaluator
SO	sulfur oxide
SO_2	sulfur dioxide
SO_x	sulfur oxides; $SO + SO_2$
TDC	top dead center; the position of the piston at the top of its stroke
T_{95}	temperature at which 95% of fuel has distilled in test method ASTM D 86
VGO	vacuum gas oil
VOC	volatile organic compound
% mass	percent by mass
% vol	percent by volume

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